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SIMULATION AND EXPERIMENTAL VALIDATION OF
RADICAL POLYMERIZATION WITH AIBN INITIATOR IN
PRESENCE OF SHEAR

*A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of*

MASTER OF TECHNOLOGY

1990

by

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to the

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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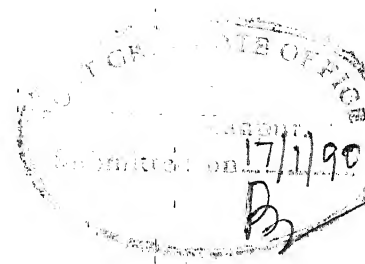
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CERTIFICATE



This is to certify that the work 'Simulation and experimental validation of radical polymerization with AIBN initiator in presence of shear ' has been carried out by Mr.G.Venkateswaran under my supervision and that this work has not been presented elsewhere for a degree.

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ACKNOWLEDGEMENTS

I take this opportunity to express my heartfelt gratitude to my thesis supervisor Dr. Anil Kumar. I thank him for his encouragement and advice, without which this work would not have been possible.

My thanks are also due to Mr. Chakraborty, Mr. Ranjit Singh and Mr. B. Sharma for the help rendered during experimentation.

I remember with thanks, all my friends, especially Devesh and Sampath for having given me a memorable time during my stay at I.I.T., Kanpur.

Lastly, I wish to thank Mr. N. K. Metia and Mr. J. R. Sharma for their excellent typing.

G. Venkateswaran

ABSTRACT

The effect of shear on the rate of polymerization of styrene in presence of activated carbon has been studied . It was found that the rate of polymerization decreases in presence of shear and is enhanced in presence of activated carbon . Based on the chemistry, a kinetic model has been proposed in which carbon is participating in the polymerization and is found to describe the experimental results well. We have also carried out simulation of free radical polymerization. Analytical expressions for isothermal polymerization have been developed for monomer and polymer concentrations and for moments of radical and dead polymer distributions in terms of a dimensionless variable Z . The analytical solution has later been adopted for nonisothermal polymerization in presence of gel effect .

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NOMENCLATURE

A, B	terms in D_0 equation (Table 11)
C_1, C_2	Constants in Q_1 equation (eqn 36)
C^*	Constant in Q_2 equation (eqn 48)
C_p	Specific heat at constant pressure
D	inside diameter of reactor
E_d, E_p, E_t	activation energies of initiation, propagation and termination reactions in absence of gel and glass effect
$E_{\theta_t}, E_{\theta_p}, E_\gamma$	energies in $\theta_t, \theta_p, \gamma$ expression (Table 11)
f	initiator efficiency
ΔH_r	enthalpy of propagation reaction
I_2	initiator
$I_0(Z), I_1(Z),$ $K_0(Z), K_1(Z)$	Modified Bessel functions
K_γ^0	frequency factor in γ expression
k_{po}, k_{to}	rate constants for propagation and termination
k_d	rate constant for initiation
k_d^0, k_p^0, k_t^0	frequency factors for k_d, k_{po} and k_{to}
k_p, k_t	rate constants for propagation and termination (with gel effect)
k_{tc}, k_{td}	termination rate constants for combination and disproportionation ($k_{tc} + k_{td} = k_t$)
m	k_p/k_t
M	Monomer

M_w	Molecular weight of monomer
P_n^{\bullet}	growing radical having n repeating units
G_i	i^{th} moment of polymer radical distribution
I, I_1	primary and secondary radicals
r_p	rate of polymerization
R	universal gas constant
R_R, R_G	radius of rotor and glass cylinder
T	Temperature, K
T_{gp}	glass transition temperature of polymer, K
T_w	Temperature at wall, K
t	reaction time
U	overall heat transfer coefficient
x	related to time of polymerization
Y	related to r_p (eqn 3)
Z	dimensionless variable (eqn 13)

Greek letters

α	$\frac{(-\Delta H_r)[M]_0 m}{\rho C_p \delta U}$
β	$\frac{D \rho C_p f k_d Z_0}{\dots}$
γ	k_{tc}/k_{td}
γ	$\frac{\omega R_R}{R_G - R_R}$
ω	angular velocity

θ_t, θ_p	characteristic migration times
θ_t^0, θ_p^0	pre exponential factors for θ_t and θ_p
λ_i	i^{th} moment of dead polymer distribution
λ_{i0}	i^{th} moment of dead polymer distribution at time $t=0$
ϕ_p	volume fraction of polymer in reaction mixture
ρ_m	density of monomer
ρ_p	density of polymer
ρ_{ps}	density of polystyrene
ψ	$\frac{1 - [P]_0^*}{1 + [P]_0^*}$

Symbols

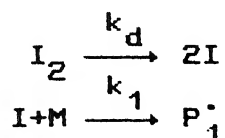
$[]$	Concentrations, gmol/lit
$[]_0$	feed concentration, gmol/lit
$[]_s$	Concentration with QSSA valid
$[]_0^*$	ratio , $\frac{[]_0}{[]_s}$

CHAPTER 1

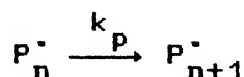
Introduction

The chain growth polymerization has been studied in detail and has been shown to consist of initiation, propagation and termination steps. These can be schematically written as

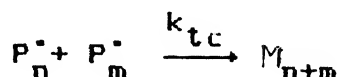
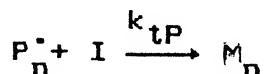
Initiation:



Propagation:



Termination:



(1)

As can be seen above, the initiation is a sequential reaction of decomposition of initiator molecules to give primary radicals and subsequent combination of primary radicals with monomer molecules. In reality all primary radicals do not produce propagating chains and they remain in 'cages' consisting of surrounding molecules before they diffuse apart. However before this diffusion takes place, the primary radicals may react with one another to form an inactive species. In order to account for this recombination, a factor called initiator efficiency, f is introduced. There are several factors which

affect the initiator efficiency and these have been discussed in the literature in detail¹⁴⁻¹⁸.

In the propagation reaction, the monomer adds on to the polymer radical and the propagation rate constant k_p has been assumed to be independent of chain length. Polymer radicals may be converted into polymer molecules by primary and mutual (combination and disproportionation) termination. The expression for rate of polymerization is obtained by making use of the standard kinetic assumption of a steady state approximation of transient species, namely, the chain radicals. Thus we obtain.

$$r_p = k_p \left[\frac{f k_d [I_2]}{(k_{tc} + k_{td})} \right]^{\frac{1}{2}} [M] \quad (2)$$

This equation is valid only for low conversions and it will be shown later that the Quasi Steady State Approximation (QSSA) breaks down due to the gel and glass effects.

A parameter y independent of monomer and initiator concentration may be defined as

$$y = \frac{r_p}{[M][I_2]^{\frac{1}{2}}} \quad (3)$$

The rate of polymerization at low conversions, in the absence of shear for several monomers have been determined experimentally and excellent compilations are available⁵. Studies have been carried out establishing the effect of mixing upon the rate of polymerization in which simple stirring devices were used. However, no correlation exists which relates the rate of polymerization with shear rates. In this work we have studied

the effect of shear on the rate of polymerization of styrene using azo iso butyronitrite (AIBN) as the initiator. We have also studied the effect of activated carbon of various particle size on the rate of polymerization.

It is well established that after certain conversion, the 'gel effect' appears as a sharp increase in the rate of reaction, usually accompanied by an increase in molecular weight and viscosity. The gel effect occurs after about 10% conversion depending on the temperature and the amount of initiator used. Numerous theoretical and experimental studies of the gel effect have been reported and it is generally agreed that it is due to the reduction in the termination rate constants, k_{tc} and k_{td} ¹⁹⁻²⁸. After a conversion of 70-80% is reached, the reaction mass becomes highly viscous and the chain propagation becomes diffusion controlled. As a result of reduction in k_p , the rate of polymerization goes down as the reaction temperature approaches the glass transition temperature of the polymerizing mixture. This behaviour is known as the glass effect²⁹⁻³³.

Most of the studies of chain growth polymerization in reactors assume isothermal reactor operation. In commercial practice however, reactors cannot be maintained in isothermal conditions. Practical problems of heat transfer and thermal runaway invariably occur.³⁴⁻⁴⁶ Because of their simplicity and low costs, tubular reactors are commercially employed and in the literature they have been theoretically as well as experimentally investigated³⁵⁻⁴².

In earlier studies of free radical polymerization, it was common to assume that the quasi steady state approximation holds.

Under this approximation, the rate of formation and rate of depletion of the polymer radicals are equal. Therefore,

$$k_t[CP]_s^2 = 2fk_d[I_2] \quad (4)$$

Here $[CP]_s$ represents the total concentration of polymer radicals with QSSA valid and $[I_2]$ is the initiator concentration. However, when gel effect sets in, k_t has been shown to decrease in value, which will result in increased $[CP]_s$ under QSSA, this way leading to higher rates of polymerization. Since all polymerization reactions are exothermic in nature, the temperature of the polymer mass would go up for the same cooling rate which in turn would give higher rate of initiation. Hence under the influence of gel effect, the upward thermal drift always occurs and the QSSA breaks down.

If the QSSA breaks down, the mole balance relation for polymer radicals $[CP]$ would be governed by a nonlinear first order differential equation instead of the simple relation given in eqn (4). The concentration $[CP]$ in the reaction mass is normally a very small number compared to the monomer or initiator concentration. As an example, for styrene polymerizing at 60°C with benzoyl peroxide initiator, $[CP]_s$ (as calculated from eqn (4)) is of the order 10^{-8} moles per liter. As a consequence in the numerical computation of $[CP]$ through its governing differential equation, the time increment Δt must be chosen very small. This would mean that the differential equations governing the performance of the tubular reactor carrying out radical polymerization are numerically extremely 'stiff' and the numerical solution is computationally time consuming.

In this work, we have written down the transient mole

balance relation for all species in the reaction mass. Assuming various rate constants for the mechanism of isothermal free radical polymerization given in eqn (1) as time independent, we develop the complete analytical solution. We have also integrated the energy balance equation making use of the above assumption. After every time step Δt we estimate the temperature, and rate constants are evaluated at the new temperature which are made use of in calculating $[M]$, $[P]$ and other quantities in the next time step. This removes the stiffness of the differential equation and results are obtained conveniently in negligibly small computation time.

CHAPTER 2

Theoretical Developments

It is possible to make mole balance for various species in the reaction mass and the batch reactor results are given in Table 1. We define concentration of polymer radicals, $[P]$ as

$$[P] = \sum_{n=1}^{\infty} [P_n] \quad (5)$$

With the help of eqn (1.2) of Table 1, one can derive an expression for the time variation of $[P]$ as below

$$\frac{d[P]}{dt} = 2fk_d[I_2] - k_t[P]^2 \quad (6)$$

When the gel and thermal effects are present in radical polymerization, the rate constants k_I and k_t are dependant on temperature and monomer conversion and therefore cannot be integrated. We will show that eqn (6) has a solution for constant k_I and k_t and then develop an analytical solution of isothermal polymerization in absence of gel effect. Subsequently we will show that these results can be naturally adopted in the presence of the gel and thermal effects.

Solution of Isothermal Radical Polymerizations

The mole balance for the initiator given in eqn (1.1) of Table 1 can be integrated for time invariant fk_d as

$$[I_2] = [I_2]_0 e^{-fk_d t} \quad (7)$$

In the above eqn, $[I_2]_0$ is the concentration of initiator at $t=0$.

Let us now transform $[P]$ in eqn (6)

$$[P] = \frac{1}{k_t} \frac{dy/dt}{y} \quad (8)$$

and upon substituting eqn (7) for $[I_2]$ in eqn (6) one obtains,

$$\frac{d^2 y}{dt^2} = 2fk_d k_t [I_2]_0 e^{-fk_d t} y \quad (9)$$

Further, we define x related to time of polymerization as

$$x = 2fk_d k_t [I_2]_0 e^{-fk_d t} \quad (10)$$

This gives

$$\frac{dx}{dt} = -fk_d \cdot x \quad (a)$$

$$\frac{dy}{dt} = \frac{dy}{dx} \frac{dx}{dt} = -fk_d \cdot x \frac{dy}{dx} \quad (b)$$

$$\frac{d^2 y}{dt^2} = \frac{d}{dx} \left(\frac{dy}{dt} \right) \frac{dx}{dt} \quad (c)$$

$$= (fk_d)^2 \cdot x \frac{dy}{dx} + (fk_d)^2 \cdot x^2 \frac{d^2 y}{dx^2} \quad (d) \quad (11)$$

In terms of these, eqn (9) becomes

$$(fk_d)^2 \cdot x^2 \frac{d^2 y}{dx^2} + (fk_d)^2 \cdot x \frac{dy}{dx} - xy = 0 \quad (12)$$

we further transform x by

$$Z = 2\sqrt{bx} \quad (a)$$

$$\text{where } b = \left(\frac{1}{fk_d} \right)^2 \quad (b) \quad (13)$$

in terms of which eqn (12) reduces to

$$Z^2 \frac{d^2 y}{dZ^2} + Z \frac{dy}{dZ} - (Z^2 - 0) y = 0 \quad (14)$$

For this y has the following solution

$$y = C_1 I_0(Z) + C_2 K_0(Z) \quad (15)$$

Where $I_0(Z)$ and $K_0(Z)$ are the modified zeroth order Bessel functions and C_1 and C_2 are the constants of integration. With the help of eqn (8), one can get $[P]$ as

$$[P] = - \frac{fk_d Z}{2k_t} \frac{1}{y} \frac{dy}{dZ} \quad (16)$$

$$= \frac{fk_d Z}{2k_t} \frac{C_2 K_1(Z) - C_1 I_1(Z)}{C_2 K_0(Z) + C_1 I_0(Z)}$$

$$= \frac{fk_d Z}{2k_t} \frac{K_1(Z) - C I_1(Z)}{K_0(Z) + C I_0(Z)} \quad (17)$$

where $C = C_1/C_2$, which is to be determined by the initial conditions

Let us assume that at $t=0$, the concentration of Polymer radicals is $[P]_0$. In the Z plane, time $t=0$ corresponds to Z_0 given by

$$Z_0 = Z \sqrt{\frac{2k_t [I_2]_0}{fk_d}} \quad (18)$$

and C in eqn (17) is given by

$$C = \frac{K_1(Z_0) - \frac{2k_t [P]_0}{fk_d Z_0} K_0(Z_0)}{I_1(Z_0) + \frac{2k_t [P]_0}{fk_d Z_0} I_0(Z_0)}$$

$$\frac{\frac{K_1(Z_0)}{I_1(Z_0)} - [P]_0^* \frac{K_0(Z_0)}{I_1(Z_0)}}{1 + [P]_0^* \frac{I_0(Z_0)}{I_1(Z_0)}} \quad (19)$$

where $[P]_0^* = \frac{[P]_0}{[P]_S} = [P]_0 \sqrt{\frac{k_t}{2fk_d [I_2]_0}} \quad (20)$

Above $[P]_S$ is the concentration of polymer radicals assuming the steady state approximation and is given by eqn (4)

The variation in the monomer concentration, $[M]$, is governed by eqn (1.3) of Table 1. We substitute eqn (13) in it to obtain

$$\frac{d[M]}{dt} = \frac{d[M]}{dz} \frac{dz}{dt} = - \frac{fk_d Z}{2} \frac{d[M]}{dz} = - k_p [M][P]$$

or

$$\frac{fk_d Z}{2} \frac{d[M]}{dz} = k_p [M] \frac{fk_d Z}{2k_t} \frac{K_1(Z) - C I_1(Z)}{K_0(Z) + C I_0(Z)}$$

$$\frac{d[M]}{dz} = [M] \frac{k_p}{k_t} \left[\frac{K_1(Z) - C I_1(Z)}{K_0(Z) + C I_0(Z)} \right] \quad (21)$$

We substitute

$$u = K_0(Z) + C I_0(Z) \quad (22)$$

which on differentiating with respect to Z gives

$$\frac{du}{dz} = -K_1(Z) + C I_1(Z) \quad (23)$$

Comparison of equations (19) and (21) gives

$$\frac{-d[M]}{[M]} \frac{k_p}{k_t} \frac{du}{u} \quad (24)$$

which on integration leads to

$$[M] = [M]_0 \left[\frac{K_0(Z) + C I_0(Z)}{K_0(Z_0) + C I_0(Z_0)} \right]^{k_p/k_t} \quad (25)$$

Above $[M]_0$ is the monomer concentration at $t=0$ (or $Z=Z_0$) and Z_0 is defined in eqn (18).

The magnitude of Z as defined in eqn (13) is very large. For example, for methyl methacrylate polymerizing at 60°C with AIBN $[I_2]_0 = 0.0258$ moles/lit] initiator, the rate constants k_d , k_p and k_t are $0.475 \times 10^{-3} \text{ min}^{-1}$, $0.4117 \times 10^5 \text{ lit/mol min}$ and $0.20383 \times 10^{10} \text{ lit/mol min}$ respectively. Taking initiator efficiency f to be 0.58, we get at time $t=0$, 'b' as defined in eqn (13) and x_0 defined by eqn (10) to be 1.3175×10^7 and 2.8756×10^4 respectively. Therefore Z at time $t=0$ is given by eqn (18) and is equal to 0.1231×10^7 . Hence the asymptotic expansion of Bessel functions valid for large arguments ($Z > 5$) may be used⁸.

Neglecting terms involving Z in the denominator, we get

$$K_1(Z) = K_0(Z) = \sqrt{\frac{\pi}{2Z}} e^{-Z}$$

$$I_1(Z) = I_0(Z) = \frac{e^Z}{\sqrt{2\pi Z}} \quad (26)$$

Making use of the above approximations for Bessel functions, C defined in eqn (19) gives

$$C = \psi \pi e^{-2Z_0} \quad \text{where } \psi = \frac{1 - [P]_0^*}{1 + [P]_0^*} \quad (27)$$

The eqn. (17) for [P] may be written as

$$P = \frac{fk_d Z}{2k_t} \frac{\frac{K_1(Z)}{I_0(Z)} - C \frac{I_1(Z)}{I_0(Z)}}{\frac{K_0(Z)}{I_0(Z)} + C}$$

After substituting for C and Bessel functions, we get an expression for the time variation of [P] as

$$[P] = \frac{fk_d Z}{2k_t} \frac{1 - \psi e^{-2(Z_0 - Z)}}{1 + \psi e^{-2(Z_0 - Z)}} \quad (28)$$

The quantities $CI_0(Z)$ and $CI_0(Z_0)$ in eqn (25) for [M] are given by

$$CI_0(Z) = \psi \pi e^{-Z_0} \frac{e^{-(Z_0 - Z)}}{\sqrt{2\pi Z}}$$

$$CI_0(Z_0) = \frac{\psi \pi e^{-Z_0}}{\sqrt{2\pi Z_0}} \quad (29)$$

These may be taken as zero, since both Z_0 and Z are of the order 10^6 . Hence the eqn (25) for [M] simplifies to

$$[M] = [M]_0 e^{-m(Z_0 - Z)} \quad (30)$$

where $m = \frac{k_p}{k_t}$

By making use of the above expressions for $[M]$ and $[P]$, we can obtain analytical expressions for various moments of radical and dead polymer distributions.

Radical and Dead Polymer Moments:

The differential equation for first moment Q_1 for radical distribution $\left[= \sum_{n=1}^{\infty} n [P_n] \right]$ can be derived from eqn.1.2 of Table 1 as follows

$$\begin{aligned} \frac{dQ_1}{dt} &= -k_t [P] Q_1 + 2fk_d [I_2] + k_p [M] \{ 2[P_1] + 3[P_2] + 4[P_3] + \dots \} \\ &\quad - k_p [M] \{ [P_1] + 2[P_2] + \dots \} \\ &= -k_t [P] Q_1 + 2fk_d [I_2] + k_p [M] \{ (1[P_1] + 2[P_2] + 3[P_3] + \dots) + \\ &\quad ([P_1] + [P_2] + [P_3] + \dots) \} \\ &\quad - k_p [M] \{ [P_1] + 2[P_2] + 3[P_3] + \dots \} \\ \frac{dQ_1}{dt} &= 2fk_d [I_2] - k_t [P] Q_1 + k_p [M] [P] \end{aligned} \quad (31)$$

The above equation is a linear differential equation of first order if we assume rate constants as time invariant. We get the integrating factor (I.F.) as follows

$$I.F = \exp \left\{ k_t \int [P] dt \right\} \quad (32)$$

Observing that

$$\frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}} = -k_p [P] dt \quad (33)$$

eqn (32) reduces to

$$\begin{aligned} I.F &= \exp \left\{ -\frac{1}{m} \ln \left(\frac{[M]}{[M]_0} \right) \right\} \\ &= \left\{ \frac{[M]}{[M]_0} \right\}^{-1/m} \end{aligned} \quad (34)$$

The integration of the differential equation (eqn 31) gives Q_1 as

$$Q_1 \left\{ \frac{[CM]}{[CM]_0} \right\}^{\frac{1}{m}} = \int (2fk_d [I_2] + k_p [M]_0 \left\{ \frac{[CM]}{[CM]_0} \right\}) [P] \left\{ \frac{[CM]}{[CM]_0} \right\}^{\frac{1}{m}} dt$$

Substituting $[I_2]$ from eqn (13) in terms of Z as

$$[I_2] = \frac{Z^2 f k_d}{8 k_t}$$

and carrying out the integration to finally obtain,

$$Q_1 = C_1 \left(\frac{[CM]}{[CM]_0} \right) + C_2 \left(\frac{[CM]}{[CM]_0} \right)^{1/m} + \frac{f k_d}{2 k_t} (Z+1) \quad (35)$$

where $C_1 = \frac{-[CM]_0}{1-1/m}$ and $C_2 = Q_{10} + \frac{[CM]_0}{1-1/m} - \frac{f k_d}{2 k_t} (Z_0+1)$ (36)

In order to derive the differential equations governing zeroth, first and second moments of dead polymer distribution, we make use of the mole balance for M_n from Table 1. We have

$$\frac{d[CM_n]}{dt} = \frac{k_{tc}}{2} \sum_{m=1}^{n-1} [P_m][P_{n-m}] + k_{td}[P_n] \sum_{n=1}^{\infty} [P_n] \quad (37)$$

Further we know that,

$$\sum_{n=2}^{\infty} n^k \sum_{m=1}^{n-1} [P_m][P_{n-m}] = \sum_{n=1}^{\infty} [P_n] \sum_{m=1}^{n-1} (m+n)^k [P_m] \quad (38)$$

The zeroth moment of dead polymer distribution $\lambda_0 = \left(\sum_n M_n \right)$ can be derived by adding eqn (37) for all n

$$\frac{d\lambda_0}{dt} = \frac{k_{tc}}{2} [P]^2 + k_{td}[P]^2 \quad (39)$$

where $[P] = \sum_{n=1}^{\infty} [P_n]$ and

eqn (38) is made use of to obtain eqn (39)

Making use of eqn (33)

$$[P] dt = \frac{-1}{k_p} \frac{d\{[CM]/[CM]_0\}}{\{[CM]/[CM]_0\}}$$

we get,

$$\int d\alpha_o = \frac{-(0.5k_{tc} + k_{td})}{k_p} \int [P] \frac{d([M]/[M]_o)}{([M]/[M]_o)}$$

From eqn (30), $\frac{d([M]/[M]_o)}{([M]/[M]_o)} = m dz$

and hence $\lambda_o - \lambda_{oo} = -\frac{(0.5k_{tc} + k_{td})m}{k_p} \int [P] dz$ (40)

Substituting for $[P]$ from eqn. (28), we get

$$\lambda_o - \lambda_{oo} = \int d\alpha_o = -(0.5 k_{tc} + k_{td}) \frac{m}{k_p} \frac{fk_d}{2k_t} \int Z \cdot \frac{1 - \psi e^{-2(Z_o - Z)}}{1 + \psi e^{-2(Z_o - Z)}} dz$$
 (41)

The rigorous evaluation of the integral leads to an infinite series and is given in Appendix I. However, if Z above is assumed to be approximately equal to Z_o , the integration in eqn (41) is considerably simplified without affecting results very much. On doing so eqn (41) leads to

$$\lambda_o - \lambda_{oo} = \int d\alpha_o = -(0.5 k_{tc} + k_{td}) \frac{m}{k_p} \frac{fk_d Z_o}{2k_t} \int \frac{1 - \psi e^{-2(Z_o - Z)}}{1 + \psi e^{-2(Z_o - Z)}} dz$$
 (42)

This can be easily integrated to

$$\lambda_o - \lambda_{oo} = \frac{(0.5k_{tc} + k_{td})}{4k_p k_t} m f k_d Z_o \left[2(Z_o - Z) - 2\ln(1 + \psi) + 2\ln(1 + \psi e^{-2(Z_o - Z)}) \right]$$
 (43)

The differential equation for first moment $\left(\lambda_1 = \sum_{n=1}^{\infty} n [M]_n \right)$

of dead polymer distribution is similarly derived using eqns (37) and (38) as follows:

$$\begin{aligned} \frac{d \sum n [M]_n}{dt} &= k_{td} [P] \sum_{n=0}^{\infty} n [P_n] + \frac{k_{tc}}{2} \sum_{n=0}^{\infty} [P_n] \sum_{m=1}^{n-1} (m + n) [P_m] \\ &= k_{td} [P] Q_1 + \frac{k_{tc}}{2} \sum_{n=0}^{\infty} [P_n] (Q_1 + n[P]) \\ &= k_{td} [P] Q_1 + \frac{k_{tc}}{2} \cdot 2Q_1 [P] \end{aligned}$$
 (44)

On eliminating [P] with the help of eqn. 1.3 of Table 1,

$$\frac{d\lambda_1}{dt} = -\frac{k_t}{k_p} \frac{Q_1}{\{[M]/[M]_0\}} \frac{d\{[M]/[M]_0\}}{dt}$$

Substituting for Q_1 , and using

$$\frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}} = m \, dZ$$

We get,

$$\lambda_1 - \lambda_{10} = -\frac{k_t}{k_p} \left[\int_1^{\{[M]/[M]_0\}} \left[C_1 + C_2 \left(\frac{[M]}{[M]_0} \right)^{\frac{1}{m} - 1} d\left(\frac{[M]}{[M]_0} \right) + \int_{Z_0}^Z \frac{fk_d}{2k_t} (Z+1) \cdot m dZ \right] \right]_{t=0}$$

where λ_{10} is the value of λ_1 at time $t=0$ and C_1 and C_2 are as defined in eqn (36)

On integrating, we obtain,

$$\lambda_1 - \lambda_{10} = \frac{k_t}{k_p} \left[C_1 \left(1 - \frac{[M]}{[M]_0} \right) + m C_2 \left(1 - \left(\frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \right] + \frac{fk_d}{2k_t} \left[\frac{1}{2} (Z_0^2 - Z^2) + (Z_0 - Z) \right] \quad (45)$$

The expression for second moment of Polymer radical distribution $Q_2 (= \sum n^2 [P_n])$ is derived making use of eqn (1.2) of Table 1, to obtain

$$\begin{aligned} \frac{dQ_2}{dt} &= -k_t [P] Q_2 + 2fk_d [I_2] + k_p [M] (2^2 [P_1] + 3^2 [P_2] + 4^2 [P_3] + \dots) \\ &\quad - k_p M ([P_1] + 2^2 [P_2] + 3^2 [P_3] + \dots) \\ &= -k_t [P] Q_2 + 2fk_d [I_2] + k_p [M] (1^2 [P_1] + 2^2 [P_2] + 3^2 [P_3] + \dots) \\ &\quad + ([P_1] + [P_2] + [P_3] + \dots) + (2.1 [P_1] + 2.2 [P_2] + \dots) - k_p [M] Q_2 \\ &= -k_t [P] Q_2 + 2fk_d [I_2] + k_p [M] (2Q_1 + [P]) \end{aligned} \quad (46)$$

This is again a linear differential equation of first order.

As before we get the integrating factor to be equal to $\left(\frac{[CM]}{[CM]_0}\right)^{-\frac{1}{m}}$, and hence

$$Q_2 \left(\frac{[CM]}{[CM]_0}\right)^{-\frac{1}{m}} = \int \left(\frac{[CM]}{[CM]_0}\right)^{-\frac{1}{m}} \left[2fk_d [I_2] + 2k_p [M_0] \left(\frac{[CM]}{[CM]_0}\right) Q_1 + b_p [M_0] [CP] \right] dt + \text{constant}$$

Substituting for $[I_2]$ and Q_1 , we get

$$Q_2 \left(\frac{[CM]}{[CM]_0}\right)^{-\frac{1}{m}} = \int 2fk_d \frac{Z^2 fk_d}{8k_t} e^{(Z_0 - Z)} \frac{Z \cdot dZ}{-fk_d Z} + \int 2k_p [M_0] \left(\frac{[CM]}{[CM]_0}\right)^{-\frac{1}{m}} \left[C_1 \left(\frac{[CM]}{[CM]_0}\right) + C_2 \left(\frac{[CM]}{[CM]_0}\right)^{\frac{1}{m}} + \frac{fk_d}{2k_t} (Z+1) \right] \cdot \frac{Z \cdot dZ}{-fk_d Z} + \int \left(\frac{[CM]}{[CM]_0}\right)^{-\frac{1}{m}} d\left(\frac{[CM]}{[CM]_0}\right) + C^* \quad (47)$$

We integrate the above expression assuming $Z=Z_0$. The rigorous solution has also been derived and is presented in appendix I and we find that the results derived in the following gives results within 0.01%.

$$Q_2 = \frac{fk_d (Z+1)}{2k_t} - \frac{4k_p [CM]_0 C_1}{fk_d Z_0 (2m-1)} \left(\frac{[CM]}{[CM]_0}\right)^2 - \frac{4k_p [CM]_0 C_2}{fk_d Z_0^m} \left(\frac{[CM]}{[CM]_0}\right)^{1+\frac{1}{m}} - \frac{2k_p [CM]_0}{k_t (m-1)} \left(\frac{[CM]}{[CM]_0}\right) - \frac{2k_p [CM]_0}{k_t Z_0 (m-1)} \left(\frac{[CM]}{[CM]_0}\right) - \frac{[CM]_0}{1-1/m} \left(\frac{[CM]}{[CM]_0}\right) + C^* \left(\frac{[CM]}{[CM]_0}\right)^{\frac{1}{m}} \quad (48)$$

where C^* is evaluated using the initial condition $Q_2 = Q_{20}$ at $t=0$. Therefore we get

$$C^* = Q_{20} - \frac{fk_d (Z_0+1)}{2k_t} + \frac{4k_p [CM]_0 C_1}{fk_d Z_0 (2m-1)} + \frac{4k_p [CM]_0 C_2}{fk_d Z_0^m} + \frac{2k_p [CM]_0}{k_t (m-1)} + \frac{2k_p [CM]_0}{k_t Z_0 (m-1)} + \frac{[CM]_0}{1-1/m} \quad (49)$$

The differential equation for second moment $\lambda_2 = \sum n^2 [M_n]$ of

dead polymer distribution is derived using Mole balance relation (eqn 37) and eqn (38) as follows:

$$\begin{aligned}
 \frac{dQ_2}{dt} &= k_{td}[P]Q_2 + \frac{k_{tc}}{2} \sum n^2 \sum [P_n] [P_{m-n}] \\
 &= k_{td}[P]Q_2 + \frac{k_{tc}}{2} \sum [P_n] \sum (m^2 + n^2 + 2nm) [P_n] \\
 &= k_{td}[P]Q_2 + \frac{k_{tc}}{2} ([P]Q_2 + [P]Q_2 + 2Q_1^2) \\
 &= (k_{tc} + k_{td}) [P]Q_2 + k_{tc} Q_1^2
 \end{aligned} \tag{50}$$

We observe that

$$\begin{aligned}
 \int k_{tc} Q_1^2 dt &= \frac{-2k_{tc}}{fk_d} \int \left[C_1^2 \left(\frac{[M]}{[M]_0} \right)^2 + C_2^2 \left(\frac{[M]}{[M]_0} \right)^{\frac{2}{m}} + \left(\frac{fk_d}{2k_t} \right)^2 (Z^2 + 2Z + 1) \right. \\
 &\quad \left. + 2C_1 C_2 \left(\frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} + C_1 \left(\frac{fk_d}{k_t} \right) \left(\frac{[M]}{[M]_0} \right) (Z + 1) \right. \\
 &\quad \left. + C_2 \left(\frac{fk_d}{k_t} \right) (Z + 1) \left(\frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right] \frac{dZ}{Z}
 \end{aligned} \tag{51}$$

Integrating the above equation assuming $Z = Z_0$ in the denominator and taking it out of the integral, we get

$$\begin{aligned}
 \int k_{tc} Q_1^2 dt &= \frac{2k_{tc}}{fk_d} \left[\frac{C_1^2}{2 \ln Z_0} \left(1 - \left(\frac{[M]}{[M]_0} \right)^2 \right) + \frac{C_2^2}{2Z_0} \left(1 - \left(\frac{[M]}{[M]_0} \right)^{\frac{2}{m}} \right) \right. \\
 &\quad \left. + \left(\frac{fk_d}{2k_t} \right)^2 \left[\frac{1}{2} (Z_0^2 - Z^2) + Z(Z_0 - Z) + \ln \left(\frac{Z_0}{Z} \right) \right] \right. \\
 &\quad \left. + \frac{2C_1 C_2}{(m+1)Z_0} \left(1 - \left(\frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} \right) + \frac{C_1}{m} \frac{fk_d}{k_t} \left(1 - \left(\frac{[M]}{[M]_0} \right) \right) \right. \\
 &\quad \left. + \frac{C_1}{mZ_0} \left(\frac{fk_d}{k_t} \right) \left(1 - \left(\frac{[M]}{[M]_0} \right) \right) + \frac{C_2}{k_t} \frac{fk_d}{Z_0} \left(1 - \left(\frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \right. \\
 &\quad \left. + \frac{C_2}{k_t Z_0} \left(1 - \left(\frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \right]
 \end{aligned} \tag{52}$$

Also,

$$\int k_t [P] Q_2 dt = \frac{-k_t}{k_p} \int \frac{Q_2}{\left(\frac{[CM]}{[CM]_0}\right)} d\left(\frac{[CM]}{[CM]_0}\right)$$

Substituting Q_2 from eqn (48) and carrying out the integration assuming $Z = Z_0$ in the denominator we get

$$\begin{aligned} \int k_t [P] Q_2 dt = & \frac{k_t}{k_p} \left[\frac{mf k_d}{2k_t} \left[\frac{1}{2} (Z_0^2 - Z^2) + (Z_0 - Z) \right] - \frac{2k_p [CM]_0 C_1}{fk_d Z_0 (2m-1)} \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^2 \right) \right. \\ & - \frac{4k_p [CM]_0 C_2}{fk_d Z_0 (m+1)} \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^{1+\frac{1}{m}} \right) - \frac{2k_p [CM]_0}{k_t (m-1)} \left(1 - \left(\frac{[CM]}{[CM]_0}\right) \right) \\ & - \frac{2k_p [CM]_0}{k_t Z_0 (m-1)} \left(1 - \left(\frac{[CM]}{[CM]_0}\right) - \frac{[CM]_0}{1 - \frac{1}{m}} \left(1 - \frac{[CM]}{[CM]_0} \right) \right. \\ & \left. \left. + mC^* \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^{\frac{1}{m}} \right) \right] \right] \end{aligned} \quad (53)$$

where C^* is as defined in eqn (49)

Therefore

$$\begin{aligned} \lambda_2 - \lambda_{20} = & \frac{2k_t c}{fk_d} \left[\frac{C_1^2}{2mZ_0} \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^2 \right) + \frac{C_2^2}{2Z_0} \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^{\frac{2}{m}} \right) \right. \\ & + \left(\frac{fk_d}{2k_t} \right)^2 \left[\frac{1}{2} (Z_0^2 - Z^2) + 2(Z_0 - Z) + \ln \left(\frac{Z_0}{Z} \right) \right] \\ & + \frac{2C_1 C_2}{(m+1)Z_0} \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^{1+\frac{1}{m}} \right) + \frac{C_1}{m} \frac{fk_d}{k_t} \left(1 - \left(\frac{[CM]}{[CM]_0}\right) \right) \\ & + \frac{C_1}{mZ_0} \left(\frac{fk_d}{k_t} \right) \left(1 - \left(\frac{[CM]}{[CM]_0}\right) \right) + \frac{C_2 fk_d}{k_t} \left(1 - \left(\frac{[CM]}{[CM]_0}\right)^{\frac{1}{m}} \right) \end{aligned}$$

$$\begin{aligned}
& + \frac{C_2 f k_d}{k_t Z_o} \left[1 - \left(\frac{[CM]}{[CM]_o} \right)^{\frac{1}{m}} \right] \\
& + \frac{k_t}{k_p} \left[\frac{m f k_d}{2 k_t} \left[\frac{1}{2} (Z_o^2 - Z^2) + (Z_o - Z) \right] - \frac{2 k_p [CM]_o C_1}{f k_d Z_o (2m - 1)} \left(1 - \left(\frac{[CM]}{[CM]_o} \right)^2 \right) \right. \\
& \quad - \frac{4 k_p [CM]_o C_2}{f k_d Z_o (m + 1)} \left(1 - \left(\frac{[CM]}{[CM]_o} \right)^{1 + \frac{1}{m}} \right) - \frac{2 k_p [CM]_o}{k_t (m - 1)} \left(1 - \left(\frac{[M]}{[M]_o} \right) \right) \\
& \quad - \frac{2 k_p [CM]_o}{k_t Z_o (m - 1)} \left(1 - \left(\frac{[CM]}{[CM]_o} \right) - \frac{[CM]_o}{1 - \frac{1}{m}} \left(1 - \frac{[CM]}{[CM]_o} \right) \right. \\
& \quad \left. \left. + m C^* \left(1 - \left(\frac{[CM]}{[CM]_o} \right)^{\frac{1}{m}} \right) \right] \right] \quad (54)
\end{aligned}$$

CHAPTER 3

Computational Techniques

We have derived the analytical solution for isothermal radical polymerization in batch reactors. In order to check the consistency of these results, we have computed the various reactor parameters using 4th order Runge Kutta numerical technique and checked our results against the analytical solution.

The flow chart of the four order Runge Kutta technique is given in Figure 1 and we have varied Δt in Table 4 and seen its effect upon the numerical solution. For stable solution, we find that the time increment Δt must be about 0.0001 min. The flow chart of computation for our analytical solution is given in Fig.2. It must be observed that our analytical solution are given in terms of Z variable. For isothermal reactor there is a straight forward exponential relation. However for nonisothermal cases, there is an ambiguity in terms of properly defining Z. This arises because in general, the rate constants vary with time of polymerization. To overcome this difficulty we recall that in the Runge Kutta technique, the total time of polymerisation is divided into small incremental time. The concentration parameters, $[M]$, λ_0 , λ_1 , λ_2 , $[P]$, Q_1 and Q_2 for the next incremental time are calculated using their values at a given time. This fact has been shown in fig. ¹₁. In such computations, between the incremental time the reaction parameters are assumed to be time invariant.

For the cases when the temperature of polymerisation as well as gelation, we similarly divide the total time of

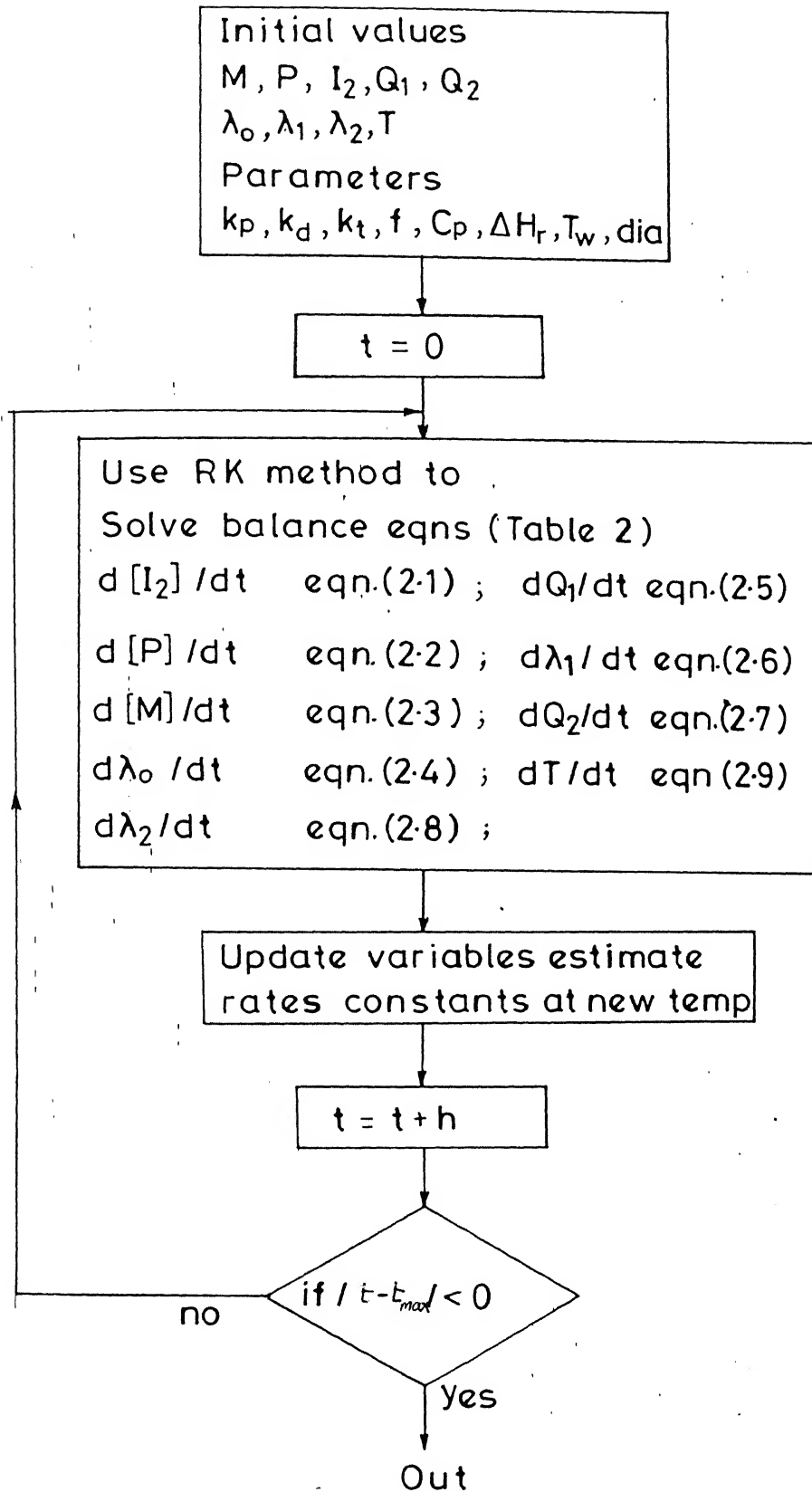


Fig.1 Runge Kutta Scheme for free radical polymerisation

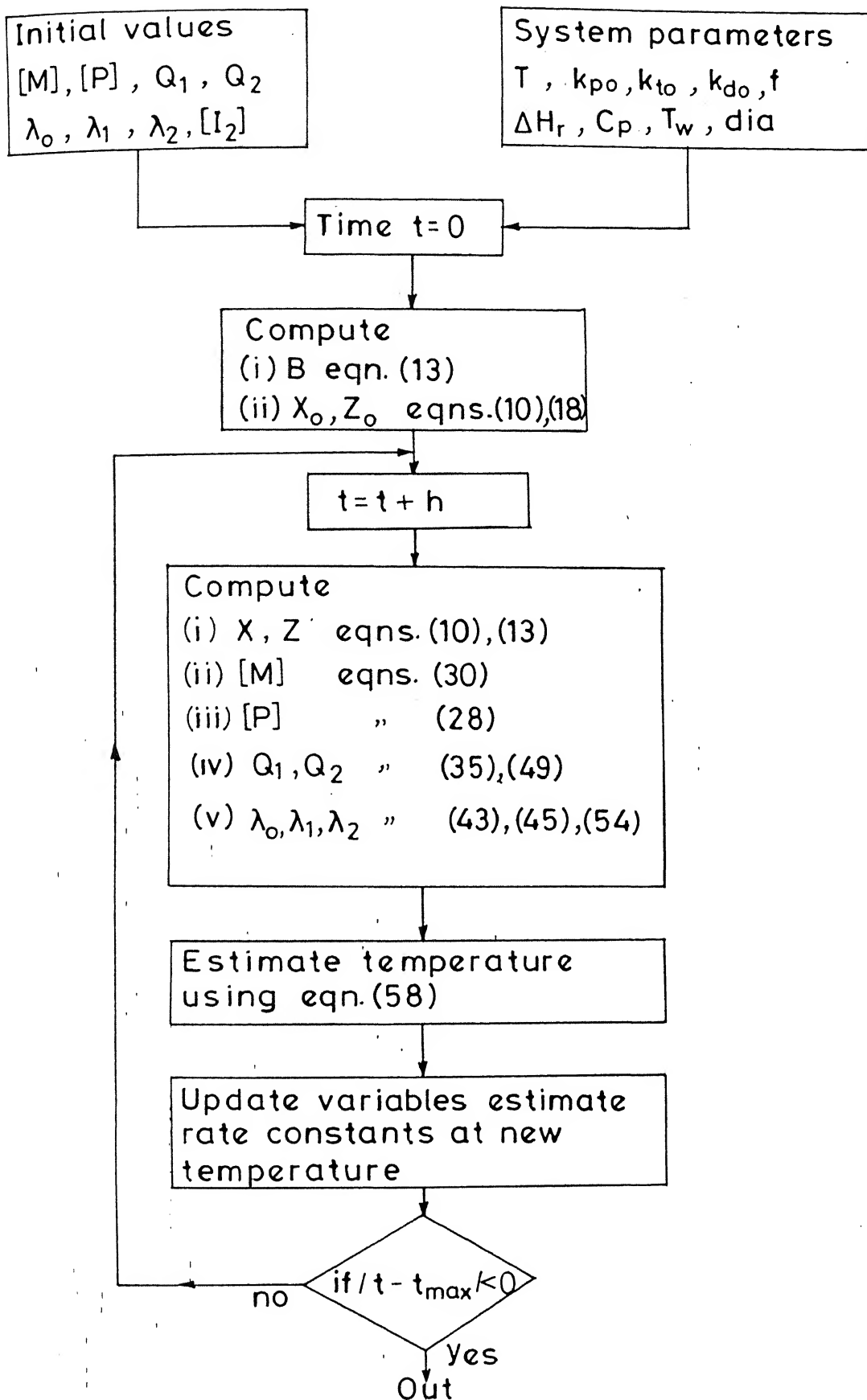


Fig.2 Analytical scheme for free radical polymerisation

polymerization into small incremental times. Between these time increments, we assume that the rate constants are time invariant. If we assume this all the results for isothermal reactors are valid, between the incremental time and only the energy balance equation remains to be integrated, which we do now.

The modelling of nonisothermal polymerization can be done by inclusion of the following energy balance,

$$\rho C_p \frac{dT}{dt} = (-\Delta H_r) k_p [M][P] - \frac{4U}{D} (T - T_w) \quad (55)$$

Here, $(-\Delta H_r)$ is the heat of the reaction, U is the heat transfer coefficient and T_w is the surrounding temperature.

The above eqn. may be rearranged using eqns. (1-3) and (30) and may be written as follows;

$$\frac{dy}{dx} + \beta y = \alpha e^{-mx} \quad (56)$$

$$\text{where } y = T - T_w \quad (a)$$

$$x = Z_o - Z \quad (b)$$

$$\beta = \frac{8U}{D \rho C_p f k_d Z_o} \quad (c)$$

$$\alpha = \frac{(-\Delta H_r) [M]_o . m}{\rho C_p} \quad (d) \quad (57)$$

The integrating factor of eqn.(56) is $e^{\beta x}$ and using the initial condition $T=T_o$ at $x=0$, we obtain the following solution.

$$T - T_w = \frac{\alpha e^{-m(Z_o - Z)}}{(\beta - m)} + (T_o - T_w) e^{-\beta(Z_o - Z)} - \frac{\alpha e^{-\beta(Z_o - Z)}}{(\beta - m)} \quad (58)$$

This result has been built in the algorithm in figure 2.

CHAPTER 4

EXPERIMENTAL

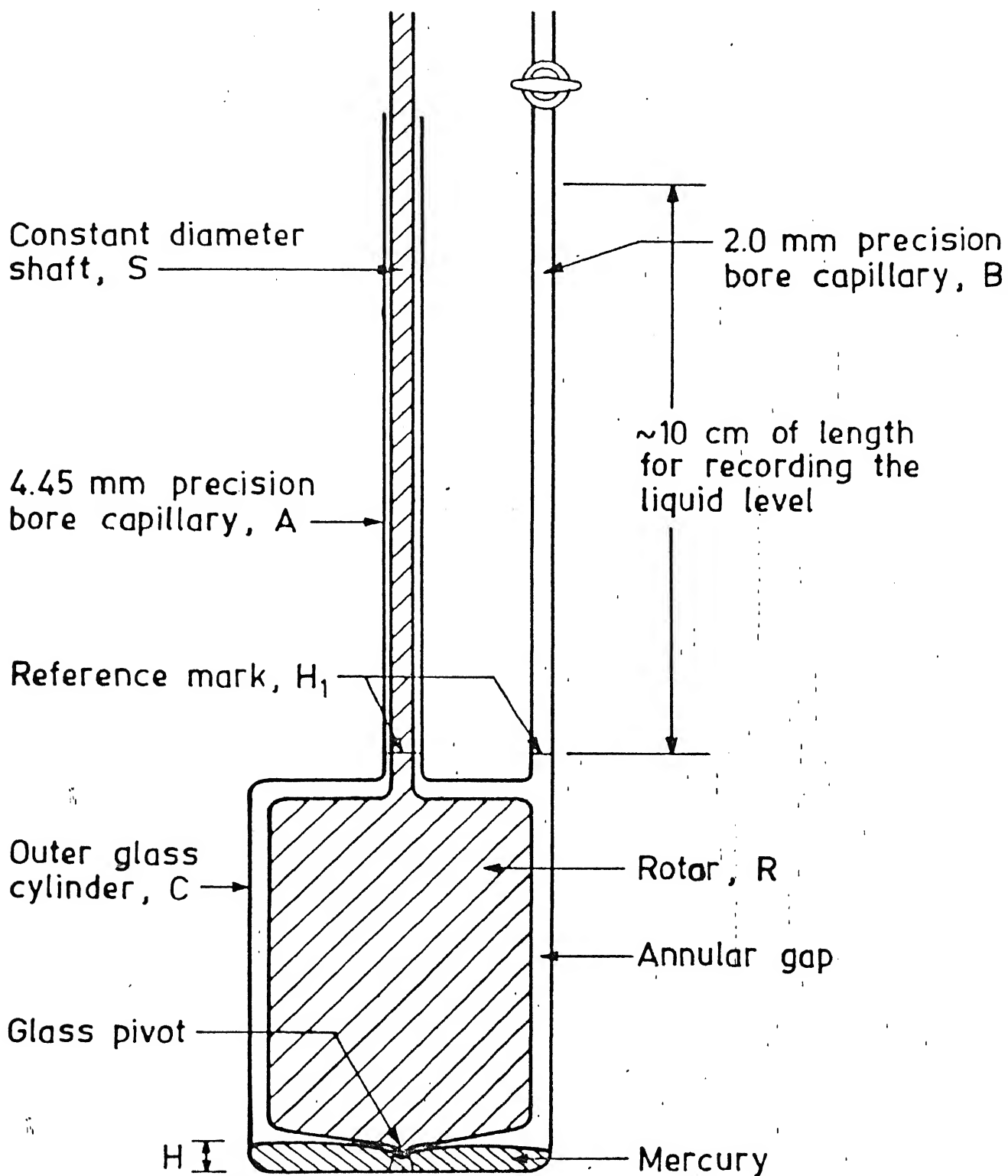
(a) Chemicals:

Analytical grade styrene (Burgoyne Burbidge & Co.) is washed with 1.0N NaOH two to three times to remove the inhibitor hydroquinone. In order to remove traces of NaOH left behind, styrene is washed thoroughly with distilled water. The washed styrene is stored over anhydrous calcium chloride atleast for two days in a defreezer, before it is used for our experiments.

The initiator used is 2-2'azo isobutyronitrile and was obtained from SAS chemicals & Co., Bombay. For further purification, it was dissolved in methanol and recrystallised before use. The activated carbon obtained from S.D. fine chemicals, was subjected to dry grinding to obtain various size ranges. Particles of size range -250 mesh and -350 mesh were used.

Dilatometer:

A sketch of special dilatometer which combines the features of an ordinary dilatometer and rheometer is shown in figure 3. The instrument consists of a glass cylinder C (I.D. 48.6 mm) having a precision bore capillary A (4.45 mm) exactly at the centre of the cylinder. A stainless steel rod of uniform thickness (o.d. 3.9 mm) passes through the capillary A and connects the rotor R (o. d. 42.5 mm) to a suitable motor. The rotor rests on a glass pivot which facilitates an easy rotation of the rotor. The precision bore capillary B (I.D. 2.0 mm) attached on the side of the cylinder C is used for filling the monomer solution in the annular space. The calibration of the dilatometer has already been done⁴.



For exact measurements, the volume of the dilatometer has to be determined at the temperature at which polymerization is to be carried out (i.e. at 60°C). However, since the coefficient of linear expansion of glass is more than 2 orders of magnitude smaller ⁽⁴⁹⁾ than the coefficient of cubic expansion of the liquid to be used, the change of the volume of the dilatometer with temperature can generally be neglected.

Procedures:

The monomer is taken in a flask and nitrogen is bubbled through it for about 3 minutes. Vacuum is applied to remove any residual nitrogen. This way we ensure that no dissolved oxygen is present in the reaction mass. The dilatometer is filled with mercury upto height H so that the reaction mixture fills only in the annular space between the rotor, and the glass vessel. The reaction mixture consisting of monomer, activated carbon and initiator with known concentration is charged to the dilatometer upto reference mark H_1 as shown in fig.3. The dilatometer is subsequently placed in a constant temperature bath which is maintained at 60°C . Immediately, the levels of the liquid in the capillaries A and B begin to rise due to the expansion of the liquid but subsequently it falls because of polymerization. The change in liquid level with time in both the capillaries A and B were measured using a cathetometer. The change in volume of the reaction mixture with time is calculated. The rotor R can be rotated at a constant speed by a suitable motor. The speed of rotation is measured by a stroboscope and is maintained at a constant value by carefully monitoring it. After polymerization, the dilatometer is emptied in the following manner. The

dilatometer is inclined carefully over a small beaker so that the mercury can run off, which is then washed with benzene and acetone and finally dried.

The rate of polymerization is calculated by standard dilatometric techniques¹. The shear rate is calculated using the rheometric equation,

$$\dot{\gamma} = \frac{\omega R_R}{R_G - R_R} \quad (59)$$

where, ω is the angular velocity of rotor, R_R and R_G are radii of rotor and cylinder respectively.

The dilatometric equation is

$$y = \frac{\rho_{Ps} \times \rho_m}{\rho_{Ps} - \rho_m} \cdot \frac{b}{M_w} \cdot \frac{1}{V} \cdot \frac{1}{[M][I_2]^{1/2}} \quad (60)$$

where, ρ_{Ps} and ρ_m are densities of polymer in solution and monomer respectively. M_w is the molecular weight of monomer, V is the volume used, $[M]$ and $[I_2]$ are the concentration of monomer and initiator respectively.

The experiment is conducted for different concentration of activated carbon and also for different size range of activated carbon.

CHAPTER 5

Results and Discussion

The earlier works of Kumar³ and Shukla⁴ have shown that the changes observed in the rate of polymerization, r_p of styrene-benzoyl peroxide system with shear, $\dot{\gamma}$ is purely due to variation of initiator efficiency.

The polymerization of styrene has been carried out in a special dilatometer as previously described. The change in height in the capillaries has been measured and converted into the change in volume of the reaction mass. Regression analysis of experimental runs has been carried out and slopes of ΔV versus time plot are used to calculate the rate of polymerization r_p . The parameter y as defined in eqn (3) has been calculated and results have been summarized in Tables 7,8,9 and 10.

We have carried out polymerization of styrene under following conditions:

- (1) Polymerization of styrene with AIBN initiator in the absence of activated carbon. *and in presence of shear*
- (2) Polymerization of styrene with AIBN initiator in presence of activated carbon (100 mg/200 ml styrene). *and in presence of shear.*
- (3) Polymerization of styrene-AIBN system in presence of different particle sizes of activated carbon. *in presence of shear.*

In order to study the effect of shear on rate of polymerization, parameter y has been defined, which is independent of monomer and initiator concentration. This has been plotted in fig.4. From theoretical considerations, we should have y independent of shear rate. Contrary to this, we find that with increase in shear rate y first goes down and then

LEGEND

- With Carbon
- Without Carbon

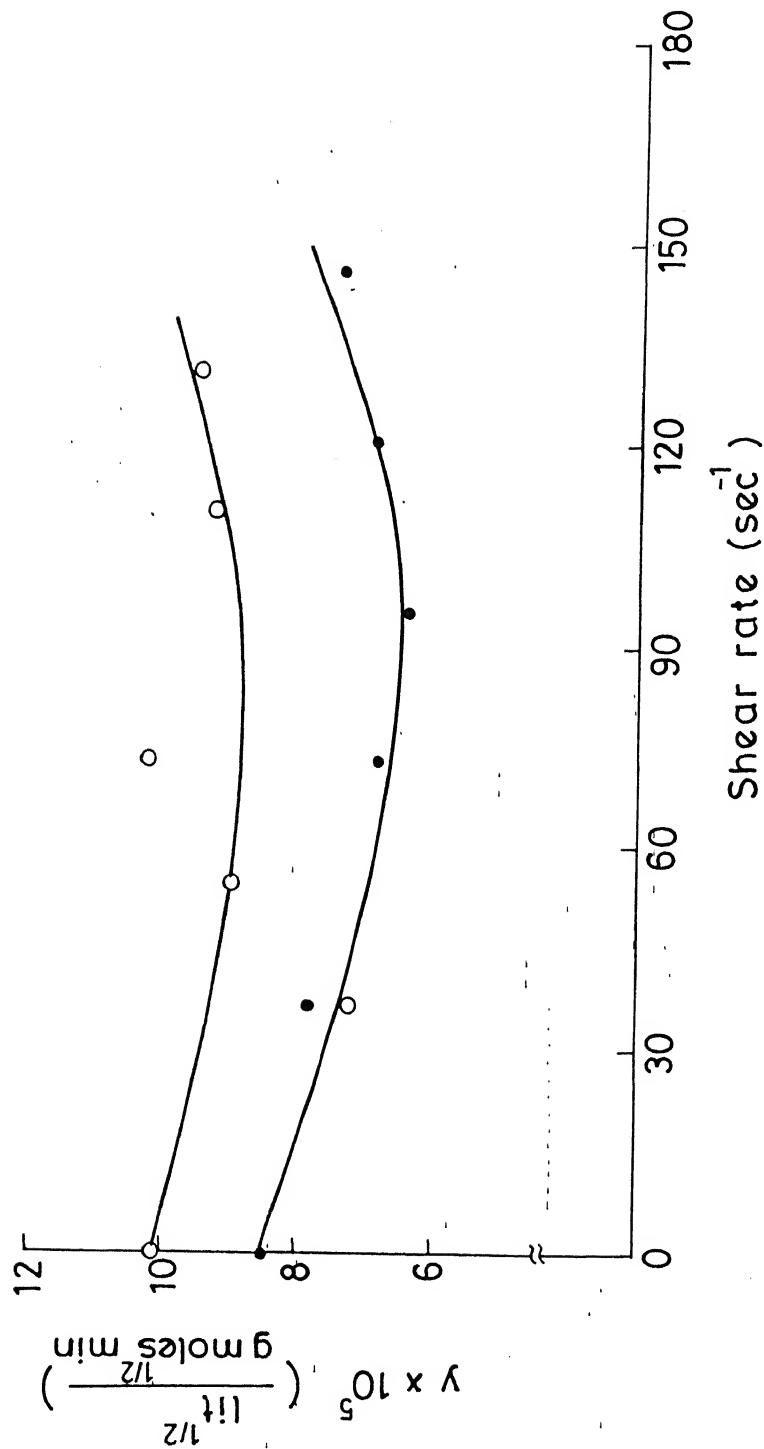
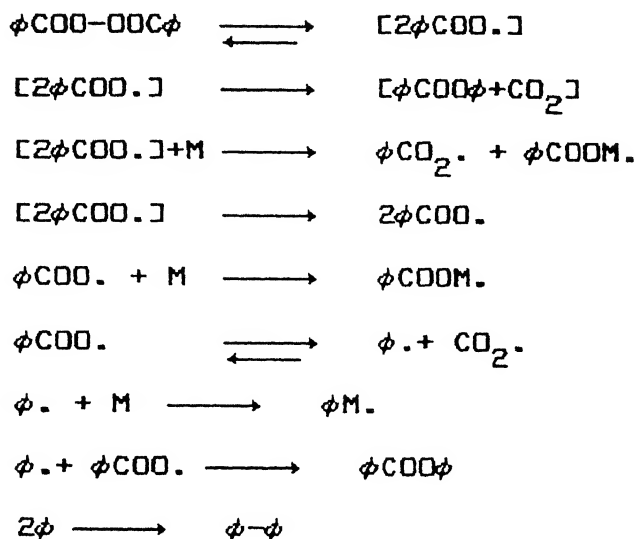


Fig.4 Variation of y with shear rate for Styrene AIBN system

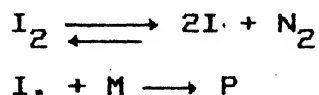
increases to about 95% of its initial value. We have conducted experiments to show that it is the initiator efficiency which is affected by shear.

The most general kinetic model for the cage effect has been discussed by Shukla⁴ and is given below:

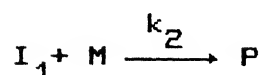
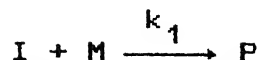
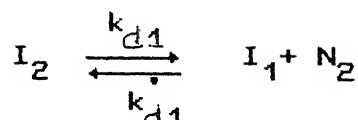
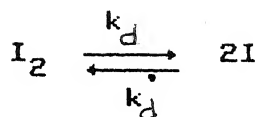


The square bracket indicates the presence of cage and ϕ represents phenyl groups formed in the decomposition of benzoyl peroxide initiator. Instead of considering this detailed model, we simplify and consider the following three idealization in the initiation step.

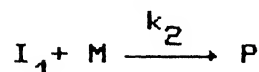
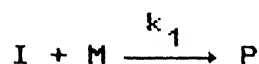
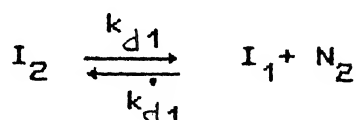
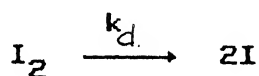
- (1) The initiator decomposes reversibly in the cage to give initiator radicals and N_2 and the radicals add on to monomer to give polymer radicals.



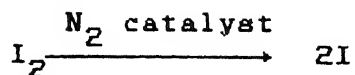
- (2) The initiator decomposes reversibly to give primary radicals from which N_2 is eliminated subsequently and both primary and secondary radicals add on to monomer to generate polymer radicals.



- (3) The same sequence of steps as above is assumed, the only difference being that the initiator decomposition is assumed to be irreversible.



In appendix 2, these kinetic schemes have been considered and analytical expressions for the rate of polymerization have been derived. If we assume that the reactivities of monomer with primary radicals are comparable to k_p and those of k_{d1} and k_{d1}^{\cdot} are comparable to k_d and k_d^{\cdot} , it can then be shown that there is negligible effect of N_2 concentration upon f . This suggests that models on cage effect alone are unable to explain the phenomenon experimentally observed. The fall in the rate of polymerization (and a subsequent rise) suggests that the N_2 gas dissolved in the reaction mass must be acting as a catalyst on the formation of primary radicals as follows:



The rate of polymerization can then be derived as

$$r_p = k_p \left\{ \frac{fk_d [N_2] [I_2]}{k_t} \right\}^{1/2} [M]$$

On the application of shear the concentration of N_2 falls due to enhanced mass transfer. As a result the rate of polymerization falls as shown by above equation. However, for large shear, the cages present initially are destroyed and the initiator efficiency recovers as has been observed experimentally.

We have carried out experiments in presence of activated carbon and we find that the rate of polymerization is increased in its presence. We notice that the activated carbon, has a distribution of particle size and we decided to separate them into -350 and -250 mesh screens. Subsequently we activated them by putting them in oven for 4 hours. In figure 5, we find that the smaller the particle size the larger is the rate of reaction and hence y_0 value. We also examined the polymerization of styrene in presence of carbon as well as the shear rate. When shear is applied the rate of polymerization falls down. In presence of carbon, when shear is applied a similar behaviour is observed except that rate of polymerization is higher in presence of carbon at a given shear rate.

There have been several studies involving activated carbon in the past and these studies focussed on fixing styrene polymer chain to carbon particles. The affixing of styrene chain on carbon particles can occur only when carbon particle was participating in the process of polymerization. Based upon the this we propose that when a given carbon particle is bombarded

LEGEND

- 350 mesh size
- △-250 mesh size

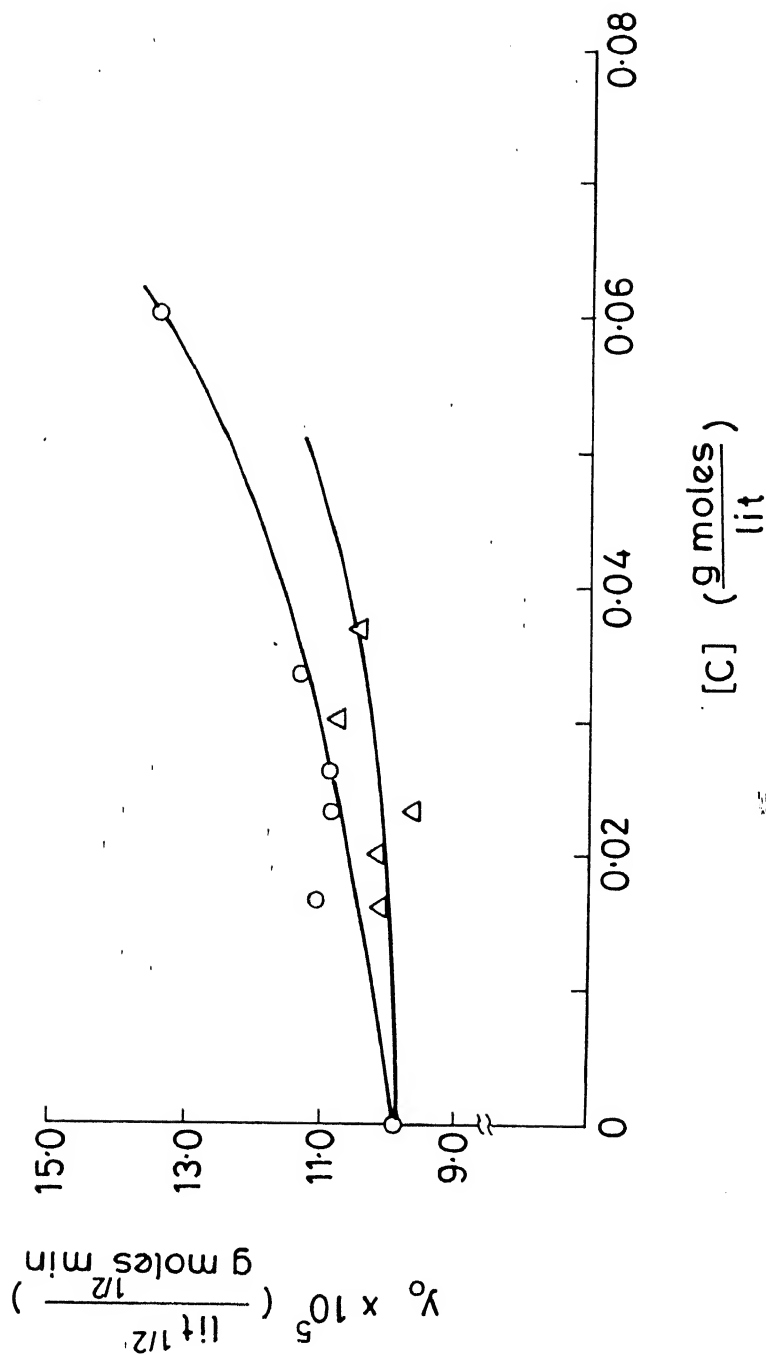
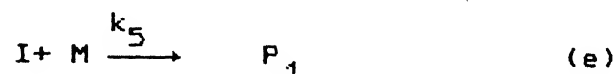
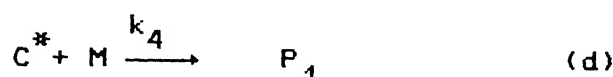
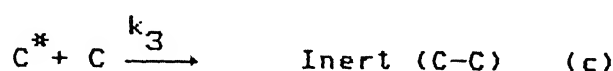
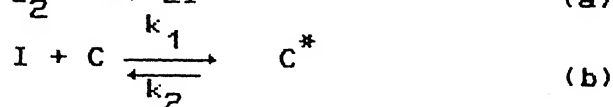


Fig.5 Variation of y_0 with activated Carbon Concentration for Styrene AIBN-system

with an initiator radical it forms some kind of an activated species $[C^*]$. We propose that this activated species can react with another carbon to form an inert molecule or can react with a monomer to give a grafted polymer molecule. In presence of carbon, the mechanism of polymerization can then be written as

Initiation:



Propagation



Termination



The derivation of rate of polymerization in presence of carbon has been given in appendix 3, and the following expression has been derived.

$$\frac{1}{r_p - r_{po}} = \frac{K_1^*}{[C]} + K_2^* \quad (62)$$

where K_1^* and K_2^* are constants dependent on temperature, monomer and initiator concentration as follows

$$K_1^* = \frac{k_2 + k_4[M]}{\frac{k_1 k_4 k_d}{k_5}} \quad (a)$$

$$K_2^* = \frac{k_3}{\frac{k_1 k_4 k_d}{k_5} [I_2][M]} \quad (b) \quad (63)$$

For the two particle size activated carbon, we have carried this exercise in Fig.6. We find that we can well represent the data by straight-line according to eqn.(62) and the constants K_1^* and K_2^* are different for different particle sizes.

We have considered the batch reactor simulation of radical polymerization. The basic differential equations governing this are given in Table 2. The numerical integration of radical polymerization is difficult for the following reason. It may be recalled that the molar concentration of intermediate polymer radicals is of the order of 10^{-8} . As opposed to this the monomer concentration is of the order of 10 while the reactor temperature is of the order of 10^2 . Due to wide variation in the ranges of various reactor parameters, the differential equations of Table 2 are numerically 'stiff' in nature and require selection of very small time increment Δt . In order to remove this numerical stiffness, we have attempted in this thesis, to determine an analytical solution of radical polymerization in batch reactors.

We have assumed the reactor to be isothermal and transformed the mole balance of polymer radicals into Z domain and have successfully obtained the analytical result. Since the value of Z is very large it was possible to develop an approximation in eqn.(28). The testing of this relation with those of Runge-Kutta numerical result are given in Table 5 and is seen that both results are almost identical for the entire range.

For nonisothermal case, we divide the total time of

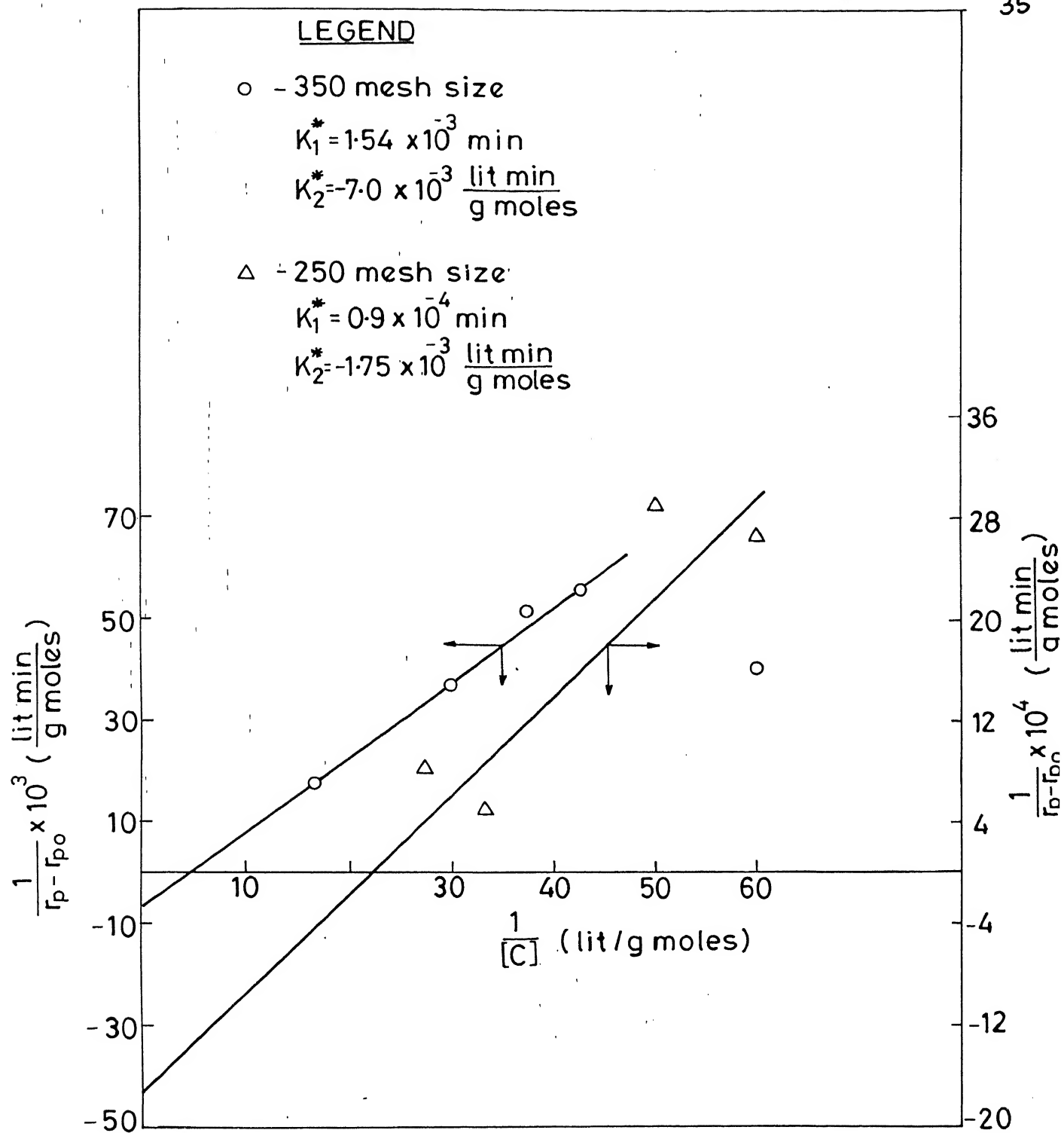


Fig.6 Plot of $\frac{1}{r_p - r_{po}}$ versus $\frac{1}{[C]}$

polymerization into small incremental time. Between this incremental time we assume the reactor performance as isothermal and use the analytical solution of the reactor developed so far. The integration of the energy equation has been done in eqn.(58) and the algorithm has been described in figure 2. With this algorithm, the results have been computed and summarized in Table 6. In the same Table the numerical results obtained from Runge-Kutta technique are also given. We find on comparison that both results are close to within 1% in the entire time range.

CHAPTER 6

CONCLUSIONS

In this work, we have studied the effect of shear on the rate of polymerization of styrene. It was observed that r_p decreases on application of shear and then partly recovers. We have considered several models of initiator efficiency and on careful examination we find that none of these can explain the experimental observation in the entire range. It is then suggested that N_2 evolved in the decomposition of initiator has a catalytic effect on the addition of monomeric units. The application of shear helps removal of N_2 from the reaction mass with a consequent fall in r_p . At high shear rate there is a likelihood that the evolved N_2 is unable to disengage from the reaction mass. As a consequence the rate of polymerization goes up due to higher concentration of N_2 in the reaction mass. From the past studies, it is known that in presence of activated carbon, the latter participates in the initiation step of polymerization. We have consequently developed a kinetic model in which carbon participates in the polymerization. The model suggests that the specific surface area of carbon is important, which would in turn mean that small particle size of carbon would give higher activity. We separated commercially available activated carbon into -250 and -350 mesh particles and we find that the latter exhibits higher activity, this way confirming the proposed kinetic model.

Simulation of free radical polymerization has also been carried out. The nonlinear differential equation for $[P]$ has been reduced to a form which has its solution in terms of Bessel function, by a suitable transformation. Analytical expressions have been derived for various moments for the case of isothermal polymerization and this has been adopted for nonisothermal polymerization in presence of gel effect.

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Appendix I

Rigorous Solution of Dead Polymer and Radical Moments

We have assumed that $Z = Z_0$ in eqns. (41) (47) and (52) in the derivation of equations for λ_0 , Q_2 and λ_2 . The rigorous solution for the above distributions, is given here.

We find that in the derivation of the equations for dead polymer and polymer radical distributions, the integral,

$$I = \int \frac{e^{-a(Z_0 - Z)}}{Z} dZ \quad (A 1.1)$$

arises naturally.

Making use of the transformation $Z_0 - Z = u$, we can write

$$\begin{aligned} I &= - \int \frac{e^{-au}}{(Z_0 - u)} du \\ &= - \frac{1}{Z_0} \left[\sum_{n=0}^{\infty} \frac{1}{Z_0^n} \int u^n e^{-au} du \right] \end{aligned} \quad (A 1.2)$$

Since

$$\int u^n e^{-au} du = e^{-au} \sum_{r=0}^n \frac{(-1)^r n!}{(n-r)! a^{r+1}} u^{n-r} \quad (A 1.3)$$

we get the integral as

$$I = e^{-a(Z_0 - Z)} \sum_{r=0}^n \frac{1}{Z_0^{n+1}} \sum_{r=0}^n \frac{n! (Z_0 - Z)^{n-r}}{(n-r)! a^{r+1}} \quad (A 1.4)$$

The zeroth moment λ_0 is therefore given by

$$\int d\lambda_0 = - \frac{(0.5k_{tc} + k_{td}) mfk_d}{2k_p k_t} \int Z \frac{1-\psi e^{-2(Z_0 - Z)}}{1+\psi e^{-2(Z_0 - Z)}} dZ + \text{Const}$$

We can write

$$\int Z \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} dZ = -Z_0 \int \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} d(Z_0-Z) \\ + \int (Z_0-Z) \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} d(Z_0-Z)$$

consider the integral,

$$\int (Z_0-Z) \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} d(Z_0-Z) \\ = \int X \frac{1-\psi e^{-2X}}{1+\psi e^{-2X}} dX$$

This can be integrated by parts by assuming

$$V = \int \frac{1-\psi e^{-2X}}{1+\psi e^{-2X}} dX \\ = \int \left[1 - \frac{2\psi e^{-2X}}{1+\psi e^{-2X}} \right] dX$$

$$V = X + \ln \left[1 + \psi e^{-2X} \right] \quad (\text{A } 1.5)$$

$$\int V du = \int \left[X + \ln \left(1 + \psi e^{-2X} \right) \right] dX$$

However, we know that

$$\int \frac{\ln(a + bX)}{X} dX$$

cannot be expressed as a finite combination of elementary functions⁷. Therefore we express the term involving logarithmic function as a series

$$\therefore \ln(1 + Y) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{Y^n}{n}$$

where $Y = \psi e^{-2X}$

Therefore

$$\begin{aligned} \int V du &= \frac{X^2}{2} + \int \left(\psi e^{-2X} - \frac{\psi^2 e^{-4X}}{2} + \frac{\psi^3 e^{-6X}}{3} - \dots \right) dX \\ &= \frac{X^2}{2} + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2nX}}{2n^2} \end{aligned} \quad (A 1.6)$$

Hence we get

$$\int X \frac{1-\psi e^{-2X}}{1+\psi e^{-2X}} dX = \frac{X^2}{2} + X \ln(1+\psi e^{-2X}) - \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2nX}}{2n^2} \quad (A1.7)$$

It is also seen that

$$\begin{aligned} -Z_0 \int \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} d(Z_0-Z) &= -Z_0 V \\ &= -Z_0 \left(X + \ln(1 + \psi e^{-2X}) \right) \end{aligned} \quad (A 1.8)$$

writing

$$\Delta = (0.5k_{tc} + k_{td}) \frac{m f k_d}{2 k_p k_t}$$

we have

$$\lambda_0 = \Delta \left[\frac{1}{2} (Z_0^2 - Z^2) + Z \ln(1 + \psi e^{-2(Z_0-Z)}) + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2n(Z_0-Z)}}{2n^2} \right] + C_1 \quad (A1.9)$$

where C_1 is the constant of integration to be evaluated using the initial condition, $\lambda_0 = \lambda_{00}$ at $t=0$ (or $Z = Z_0$)

We get,

$$C_1 = \lambda_{00} - \Delta \left[Z_0 \ln(1 + \psi) + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n}{2n^2} \right]$$

Hence we finally obtain

$$\lambda_0 - \lambda_{00} = \Delta \left[\frac{1}{2} (Z_0^2 - Z^2) + \ln \left\{ \frac{(1+\psi e^{-2(Z_0-Z)})^Z}{(1+\psi)^{Z_0}} \right\} - \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n}{2n^2} \left(1 - e^{-2n(Z_0-Z)} \right) \right]$$

(A1.10)

The equation for second moment of polymer radical distribution (from Eqn (46)) is

$$Q_2 \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} = \int \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} \left[2fk_d [I_2] + 2k_p [M] Q_1 + k_p [M] [P] \right] dt$$

This can be split into three integrals, as

$$Q_2 \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} = \int 2fk_d [I_2] \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} dt + \int 2k_p [M] Q_1 \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} dt + \int \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} k_p [M] [P] dt \quad (A 1.11)$$

The first integral I_1 gives

$$I_1 = \frac{fk_d}{2k_t} (Z + 1) \quad (A 1.12)$$

The second integral I_2 is

$$I_2 = \int \left(\frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} \left[2k_p [M]_0 C_1 \left(\frac{[M]}{[M]_0} \right)^2 + 2k_p [M]_0 C_2 \left(\frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} + \frac{fk_d}{2k_t} (Z+1) 2k_p [M]_0 \left(\frac{[M]}{[M]_0} \right) \right] dt$$

Expressing $\left(\frac{[M]}{[M]_0} \right)$ in terms of $(Z_0 - Z)$ and making use of eqn (A1.4) and dividing by integrating factor, we obtain for the second integral

$$\begin{aligned}
I_2 = & - \frac{4k_p [M]_0 C_1}{fk_d} e^{-2m(Z_0 - Z)} \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^n \frac{n! (Z_0 - Z)^{n-r}}{(n-r)! (2m-1)^{r+1}} \\
& - \frac{4k_p [M]_0 C_2}{fk_d} e^{-(m+1)(Z_0 - Z)} \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^n \frac{n! (Z_0 - Z)^{n-r}}{(n-r)! m^{r+1}} \\
& - \frac{2k_p [M]_0}{k_t} \left[\frac{e^{-(m)(Z_0 - Z)}}{(m-1)} \right] \\
& - \frac{2k_p [M]_0}{k_t} e^{-(m)(Z_0 - Z)} \sum_{n=0}^{\infty} \frac{1}{Z_0^n} \sum_{r=0}^n \frac{n! (Z_0 - Z)^{n-r}}{(n-r)! (m-1)^{r+1}} \quad (A1.13)
\end{aligned}$$

Similarly the third Integral I_3 is

$$I_3 = - \frac{[M]_0}{1 - \frac{1}{m}} \left(\frac{[M]}{[M]_0} \right) \quad (A 1.14)$$

For the sake of convenience, let

$$\sum^Z (X) = \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^n \frac{n! (Z_0 - Z)^{n-r}}{(n-r)! X^{r+1}} \quad (A 1.15)$$

Then

$$\begin{aligned}
Q_2 = & \frac{fk_d}{2k_t} (Z+1) - \frac{4k_p [M]_0 C_1}{fk_d} e^{-2m(Z_0 - Z)} \sum^Z (2m-1) \\
& - \frac{4k_p [M]_0 C_2}{fk_d} e^{-(m+1)(Z_0 - Z)} \sum^Z (m) - \frac{2k_p [M]_0}{k_t (m-1)} \left(\frac{[M]}{[M]_0} \right) \\
& - \frac{2k_p [M]_0}{k_t} e^{-(m)(Z_0 - Z)} \sum^Z (m-1) - \frac{[M]_0}{1 - \frac{1}{m}} \left(\frac{[M]}{[M]_0} \right) + C_2^* \left(\frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \quad (A 1.16)
\end{aligned}$$

$$Q_2 = Q_{20} \text{ at } Z = Z_0$$

$$\therefore C_2^* = Q_{20} - \frac{fk_d}{2k_t} (Z_0 + 1) + \frac{2k_p [M]_0}{k_t (m-1)} + \frac{[M]_0}{1 - \frac{1}{m}} \quad (A 1.17)$$

The differential equation governing second moment of dead polymer distribution (eqn 50) is

$$\frac{dQ_2}{dt} = k_t [P] Q_2 + k_{tc} Q_1^2$$

Integrating eqn (51) using eqn (A 1.4) and eqn (30) we obtain on substituting the limits

$$\begin{aligned} \int k_t c Q_1^2 dt = & \frac{2k_t c}{fk_d} \left[\left(\frac{fk_d}{2k_t} \right)^2 \left\{ \frac{1}{2} (Z_o^2 - Z^2) + Z(Z_o - Z) + \ln(Z_o - Z) \right\} \right. \\ & - C_1^2 e^{-2m(Z_o - Z)} \sum_{(2m)}^2 + C_2^2 e^{-2(Z_o - Z)} \sum_{(2)}^2 \\ & + C_1 \left(\frac{fk_d}{k_t} \right) \frac{1}{m} (1 - e^{-m(Z_o - Z)}) - C_1 \left(\frac{fk_d}{k_t} \right) e^{-m(Z_o - Z)} \sum_{(m)}^2 \\ & \left. + C_2 \left(\frac{fk_d}{k_t} \right) (1 - e^{-(Z_o - Z)}) - C_2 \left(\frac{fk_d}{k_t} \right) e^{-(Z_o - Z)} \sum_{(1)}^2 \right] \quad (A 1.18) \end{aligned}$$

Further

$$\begin{aligned} \int k_t [P] Q_2 dt &= - \frac{k_t}{k_p} \int \frac{Q_2}{\left(\frac{[M]}{[M]_o} \right)} d \left(\frac{[M]}{[M]_o} \right) \\ &= - \frac{k_t}{k_p} \int \frac{Q_2}{\left(\frac{[M]}{[M]_o} \right)^m} \left(\frac{[M]}{[M]_o} \right) dZ \\ &= - \int Q_2 dZ \end{aligned}$$

Integrating eqn (A 1.16) using eqn (A 1.4) we get,

$$\begin{aligned} \int k_t [P] Q_2 dt = & \frac{fk_d}{2k_t} \left[\frac{1}{2} (Z_o^2 - Z^2) + Z(Z_o - Z) \right] - \frac{3[M]_o}{(m-1)} (1 - e^{-m(Z_o - Z)}) \\ & + \frac{2k_p [M]_o}{k_t} e^{-m(Z_o - Z)} \sum_{(m-1, m)}^3 + \frac{4k_p [M]_o C_1}{fk_d} \sum_{(2m-1, 2m)}^3 \\ & + \frac{4k_p [M]_o C_2}{fk_d} e^{-(m+1)(Z_o - Z)} \sum_{(m, m+1)}^3 + C_2^* (1 - e^{-(Z_o - Z)}) \quad (A 1.19) \end{aligned}$$

Where C_2^* is as defined in eqn (A 1.17) and

$$\sum^3 (X, Y) = \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^n \frac{n!}{(n-r)! X^{r+1}} \sum_{p=0}^{n-r} \frac{(n-r)! (Z_0 - Z)^{n-r-p}}{(n-r-p)! Y^{p+1}} \quad (A1.20)$$

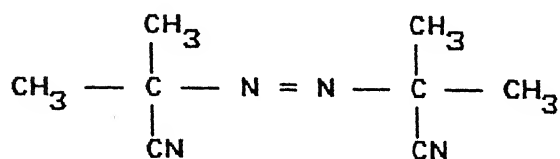
Therefore,

$$\begin{aligned} \lambda_2 - \lambda_{20} = & \frac{2k_{tc}}{fk_d} \left[\left(\frac{fk_d}{2k_t} \right)^2 \left\{ \frac{1}{2} (Z_0^2 - Z^2) + 2(Z_0 - Z) + \ln(Z_0 - Z) \right\} \right. \\ & - C_1^2 e^{-2m(Z_0 - Z)} \sum^2 (2m) - C_2^2 e^{-2(Z_0 - Z)} \sum^2 (2) \\ & + C_1 \left(\frac{fk_d}{2k_t} \right) \frac{1}{m} (1 - e^{-m(Z_0 - Z)}) - C_1 \left(\frac{fk_d}{k_t} \right) e^{-m(Z_0 - Z)} \sum^2 (m) \\ & \left. + C_2 \left(\frac{fk_d}{k_t} \right) (1 - e^{-(Z_0 - Z)}) - C_2 \left(\frac{fk_d}{k_t} \right) e^{-(Z_0 - Z)} \sum^2 (1) \right] \\ & + \frac{fk_d}{2k_t} \left[\frac{1}{2} (Z_0^2 - Z^2) + 2(Z_0 - Z) \right] - \frac{3[CM]_0 (1 - e^{-m(Z_0 - Z)})}{(m-1)} \\ & + \frac{4k_p [CM]_0 C_1}{fk_d} e^{-2m(Z_0 - Z)} \sum^3 (2m-1, 2m) \\ & - \frac{4k_p [CM]_0 C_2}{fk_d} e^{-(m+1)(Z_0 - Z)} \sum^3 (m, m+1) \\ & + \frac{2k_p [CM]_0 e^{-m(Z_0 - Z)}}{k_t} \sum^3 (m-1, m) + C_2^* (1 - e^{-(Z_0 - Z)}) \end{aligned} \quad (A 1.21)$$

APPENDIX 2

Various kinetic models

The bulk polymerization of styrene is carried out in presence of 2,2'-azoisobutyronitrile (AIBN) having the following structure



2,2' azoisobutyronitrile

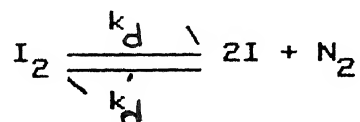
This is stable at room temperature, but decompose thermally above 40°C giving substituted alkyl radicals and nitrogen. The radicals remain in a 'cage' before they diffuse apart, and during this time a recombination of radicals may take place. In order to account for this, the initiator efficiency 'f' has been introduced.

We have modelled the cage effect in three different ways to explain the effect of shear upon initiator efficiency 'f' and finally show that the evolved N₂ has a catalytic effect in order to explain the decrease in rate of polymerization of styrene on application of shear.

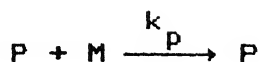
MODEL 1

The following scheme is proposed:

Initiation:



Propagation:



Termination:



Balance on $[I]$ gives

$$\begin{aligned} \frac{d[I]}{dt} &= k_d [I_2] - 2k'_d [I] [N_2] - k_1 [I] [M] \\ \therefore [I] &= \frac{k_d [I_2]}{2k'_d [N_2] + k_1 [M]} \end{aligned} \quad (A\ 2.2)$$

Also

$$\frac{d[CP]}{dt} = k_1 [I] [M] - k_t [CP]^2 \quad (A\ 2.3)$$

$$\therefore k_t [CP]^2 = k_1 [M] \frac{k_d [I_2]}{2k'_d [N_2] + k_1 [M]}$$

$$[CP] = \sqrt{\frac{k_d [I_2]}{k_t}} \cdot \sqrt{\frac{k_d [M]}{2k'_d [N_2] + k_1 [M]}} \quad (A\ 2.4)$$

$$\begin{aligned} r_p &= k_p [M] [CP] = k_p [M] \sqrt{\frac{k_d [I_2]}{k_t}} \cdot \sqrt{\frac{k_d [M]}{2k'_d [N_2] + k_1 [M]}} \\ & \quad (A\ 2.5) \end{aligned}$$

However, we have from eqn (2)

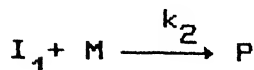
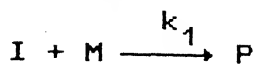
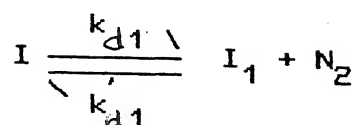
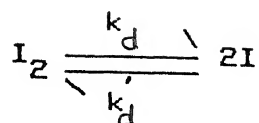
$$r_p = k_p [M] \left(\frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} f^{\frac{1}{2}}$$

Hence, on comparing the above two equations, we get

$$f = \frac{k_d [M]}{2k'_d [N_2] + k_1 [M]} \quad (A\ 2.6)$$

MODEL 2

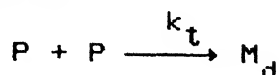
Initiation



Propagation



Termination



(A2.7)

Balance on $[I]$ gives

$$\begin{aligned} \frac{d[I]}{dt} = & k_d [I_2] - 2k_d' [I] - k_{d1} [I] \\ & + k_{d1}' [N_2] [I_1] - k_1 [I] [M] \end{aligned} \quad (A2.8)$$

Balance on $[I_1]$ gives,

$$\frac{d[I_1]}{dt} = k_{d1} [I] + k_{d1}' [N_2] [I_1] - k_2 [I_1] [M] \quad (A2.9)$$

$$\therefore [I_1] = \frac{k_{d1} [I]}{k_{d1}' [N_2] + k_2 [M]} \quad (A2.10)$$

$$\begin{aligned} k [I_2] - 2k_d' [I] - k_{d1} [I] + k_{d1}' [N_2] \frac{k_1 [I]}{k_{d1}' [N_2] + k_2 [M]} \\ - k_1 [I] [M] = 0 \end{aligned}$$

$$\therefore [I] = \frac{k_d [I_2]}{\left[2k_d' + k_{d1} + k_1 [M] - \frac{k_{d1}' k_{d1} [N_2]}{k_{d1}' [N_2] + k_2 [M]} \right]} \quad (A2.11)$$

Now,

$$\frac{d[CP]}{dt} = k_1 [I] [CM] + k_2 [I_1] [CM] - k_t [CP]^2 \quad (A 2.12)$$

$$[CP] = \left\{ k_1 [I] [CM] + k_2 [I_1] [CM] \right\}^{\frac{1}{2}} \cdot \frac{1}{k_t^{1/2}}$$

$$r_p = k_p [CM] [CP] = \frac{k_p [CM] \{k_1 [I] [CM] + k_2 [I_1] [CM]\}^{\frac{1}{2}}}{k_t^{1/2}} \quad (A2.13)$$

Let

$$X = 2k'_1 + k_1 + k_1 [CM] - \frac{k'_{d1} k_{d1} [N_2]}{k'_{d1} [N_2] + k_2 [CM]} \quad (A2.14)$$

Then

$$k_1 [I] [CM] = k_1 [CM] \cdot \frac{k_d [I_2]}{X}$$

$$k_2 [I_1] [CM] = k_2 [CM] \cdot \frac{k_1 [I]}{k'_{d1} [N_2] + k_2 [CM]}$$

$$= \frac{k_2 k_{d1} [CM]}{k'_{d1} [N_2] + k_2 [CM]} \cdot \frac{k_d [I_2]}{X} \quad (A 2.15)$$

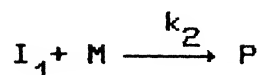
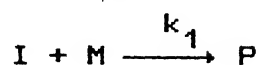
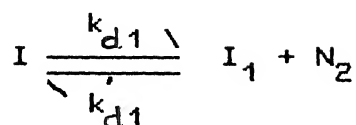
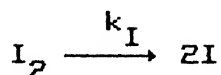
$$\therefore r_p = k_p [CM] \left(\frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} \left\{ \frac{k_1 [CM]}{X} + \frac{k_2 k_{d1} [CM]}{X [k'_{d1} [N_2] + k_2 [CM]]} \right\} \quad (A2.16)$$

Comparing the above equation with eqn (2) we get

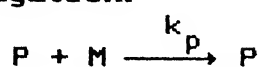
$$f = \frac{k_1 [I]}{X} + \frac{k_2 k_{d1} [CM]}{X [k'_{d1} [CO_2] + k_2 [CM]]} \quad (A 2.17)$$

Model 3

Initiation:



Propagation:



Termination:

From $[I_1]$ balance,

$$[I_1] = \frac{k_{d1}[I]}{k'_{d1}[N_2] + k_2[M]} \quad (A2.19)$$

From $[I]$ balance,

$$[I] = \frac{K_d [I_2]}{Y}$$

$$\text{where } Y = K_{d1} + k_1 [M] - \frac{K_{d1}K'_{d1}[N_2]}{k'_{d1}[N_2] + k_2 [M]} \quad (A2.20)$$

From $[P]$ balance

$$k_t [P]^2 = k_1 [I] [M] + k_2 [I_1] [M]$$

$$k_t [P]^2 = \frac{k_1 K_d [I_2] [M]}{Y} + k_2 [M] \frac{K_{d1} K_I [I_2]}{Y [k'_{d1} [N_2] + k_2 [M]]}$$

$$[P] = \left[\left(\frac{K_d [I_2]}{k_t} \right)^{\frac{1}{2}} \frac{k_1 [M]}{Y} + \frac{K_{d1} K_2 [M]}{Y [k'_{d1} [N_2] + k_2 [M]]} \right]^{\frac{1}{2}} \quad (A2.21)$$

$$r_p = k_p [M] [P]$$

$$= k_p [M] \left(\frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} \left[\frac{k_1 [M]}{Y} + \frac{K_{d1} K_2 [M]}{Y (k'_{d1} [N_2] + k_2 [M])} \right]^{\frac{1}{2}} \quad (A2.22)$$

Comparing the above equation with eqn (2) we get

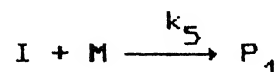
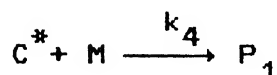
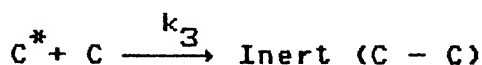
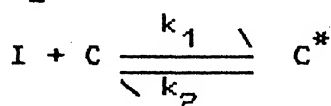
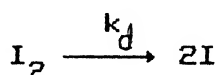
$$f = \frac{k_1 [M]}{Y} + \frac{K_{d1} K_2 [M]}{Y (k'_{d1} [N_2] + k_2 [M])} \quad (A 2.23)$$

APPENDIX 3

Model to account for the effect of activated carbon
on rate of polymerization

It has been found that the rate of polymerization goes up in the presence of activated carbon and the increase appears to depend on the specific surface area (ft^2/ft^3) of carbon particles used. The following model is put forward to explain the effect of activated carbon concentration on the rate of polymerization;

Initiation:



Propagation :



Termination :



Above C^* is an activated species formed by the reaction of primary radicals with carbon. Assuming a steady state hypothesis (S.S. hypothesis) for C^* , we get

$$k_1 [C] [I] - k_2 [C^*] - k_3 [C^*] [C] - k_4 [C^*] [M] = 0$$

$$\text{or } [C^*] = \frac{k_1 [C] [I]}{k_2 + k_3 [C] + k_4 [M]} \quad (\text{A3.2})$$

Balance on [I] gives (assuming S.S. hypothesis for intermediate species)

$$k_d [I_2] - k_1 [I] [C] + k_2 [C^*] - k_5 [I] [M] = 0$$

Further if we assume that the interaction of initiator radical and carbon particles is small in comparison to decomposition of initiator and formation of $[P_1]$ we get

$$[I] = \frac{k_d [I_2]}{k_5 [M]} \quad (A 3.3)$$

The rate of polymerization is then given by

$$r_p = k_4 [C^*] [M] + r_{po} \quad (A 3.4)$$

Where r_{po} is the rate of polymerization in absence of activated carbon.

From eqn (A3.2) we get

$$r_p - r_{po} = \frac{k_4 k_1 [C] [I] [M]}{k_2 + k_3 [C] + k_4 [M]} \quad (A 3.5)$$

$$\frac{1}{r_p - r_{po}} = \frac{k_2 + k_4 [M]}{k_1 k_4 [C] [I] [M]} + \frac{k_3}{k_1 k_4 [I] [M]}$$

On substituting for [I] from eqn (A 3.3) we get

$$\frac{1}{r_p - r_{po}} = \frac{k_2 + k_4 [M]}{\frac{k_1 k_4 k_d}{k_5} [I_2] [C]} + \frac{k_3}{\frac{k_1 k_4 k_d}{k_5} [I_2] [M]} \quad (A 3.6)$$

If only [C] is varied, with initiator and monomer concentration remaining almost the same, we can write

$$\frac{1}{r_p - r_{po}} = \frac{K_1^*}{[C]} + K_2^* \quad (A 3.7)$$

$$\text{where } K_1^* = \frac{k_2 + k_4 [M]}{\frac{k_1 k_4 k_d}{k_5}} \quad (a)$$

$$K_2^* = \frac{k_3}{\frac{k_1 k_4 k_d}{k_5} [I_2][M]} \quad (b) \quad (A 3.8)$$

A plot of $\frac{1}{r_p - r_{p0}}$ versus $\frac{1}{[C]}$ is found to be linear and is included under results and discussion.

Table 1

Mole and energy balance relation for various species in batch (or tubular) reactors carrying out Radical Polymerization

(1) Initiator, I_2

$$\frac{d[I_2]}{dt} = -fk_d[I_2] \quad (1.1)$$

(2) Growing Polymer radicals, $[P_n]$, of chain length n ($n=1,2,3,\dots$)

$$[P] = \sum_{n=1}^{\infty} [P_n]$$

$$\frac{d[P_1]}{dt} = k_I[I][M] - k_p[P_1][M] - k_t[P_1][P]$$

$$\frac{d[P_n]}{dt} = k_p[M] \left[[P_{n-1}] - [P_n] \right] - k_t[P_n][P] \quad (1.2)$$

3. Monomer, M

$$\frac{d[M]}{dt} = -k_p[P][M] \quad (1.3)$$

4. Inactive Polymer, $[M_n]$, of chain length n ($n=2,3,\dots$)

$$\frac{d[M_n]}{dt} = \frac{k_{tc}}{2} \sum_{m=1}^{n-1} [P_m][P_{n-m}] + k_{td}[P_n] \sum_{n=1}^{\infty} [P_n] \quad (1.4)$$

5. Energy balance

$$\rho C_p \frac{dT}{dt} = (-\Delta H_r)k_p [M][P] - \frac{4U}{D} (T - T_w) \quad (1.5)$$

Table 2 : Differential Equations for free radical polymerization

$$1. \quad \frac{d[I_2]}{dt} = -fk_d[I_2] \quad (2.1)$$

$$2. \quad \frac{d[CP]}{dt} = 2fk_d[I_2] - k_t[CP]^2 \quad (2.2)$$

$$3. \quad \frac{d[CM]}{dt} = -k_p[CP][CM] \quad (2.3)$$

$$4. \quad \frac{d\lambda_o}{dt} = (0.5k_{tc} + k_{td})[CP]^2 \quad (2.4)$$

$$5. \quad \frac{dQ_1}{dt} = 2fk_d[I_2] - k_t[CP]Q_1 - k_p[CM][CP] \quad (2.5)$$

$$6. \quad \frac{d\lambda_1}{dt} = (k_{tc} + k_{td})[CP]Q_1 \quad (2.6)$$

$$7. \quad \frac{dQ_2}{dt} = 2fk_d[I_2] + k_p[CM](2Q_1 + [CP]) - k_t[CP]Q_2 \quad (2.7)$$

$$8. \quad \frac{d\lambda_2}{dt} = (k_{tc} + k_{td})[CP]Q_2 + k_{tc}Q_1^2 \quad (2.8)$$

$$9. \quad \frac{dT}{dt} = \frac{(-\Delta H_r)k_p[CM][CP]}{\rho C_p} - \frac{4U}{D\phi C_p} (T - T_w) \quad (2.9)$$

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Table 3 : Rate constants and other parameters for PMMA

A	=	$0.168 - 8.21 \times 10^{-6} (T - T_{gp})^2$
B	=	0.03
C _p	=	0.4 cal/gm°C
E _d	=	30.66 Kcal/mole
E _p	=	4.35 Kcal/mole
E _t	=	0.701 Kcal/mole
E _γ	=	4.09 Kcal/mole
E _{θp}	=	28.2 Kcal/mole
E _{θt}	=	34.4 Kcal/mole
f	=	0.58
$\bar{\Delta H}_r$	=	13.9 Kcal/mol
k _d ^o	=	$6.32 \times 10^{16} \text{ min}^{-1}$
k _t ^o	=	$5.88 \times 10^9 \text{ lit/mol min}$
k _p ^o	=	$2.95 \times 10^7 \text{ lit/mol min}$
k _γ ^o	=	3.956×10^{-4}
T _{gp}	=	387 K
θ _p ^o	=	$5.4814 \times 10^{-16} \text{ min}$
θ _t ^o	=	$1.1553 \times 10^{-227} \text{ mol-min/lit}$
ρ _m	=	$0.9665 - 0.0011 (T - 273) \text{ gm/cm}^3$
ρ _p	=	1.2 gm/cm^3
[I ₂] _o	=	0.0258 gmoles/lit
[M] _o	=	8.9334 gmoles/lit

Table 4 : Stable time step for fourth order Runge Kutta Method

Time (min)	$\Delta t=0.02\text{min}$		$\Delta t=0.01\text{ min}$		$\Delta t=0.005\text{ min}$		$\Delta t=0.0001\text{ min}$	
	$[P] \lambda_o$	$[P] \times 10^7$	$\lambda_o \times 10^4$		$[P] \times 10^7$	$\lambda_o \times 10^4$	$[P] \times 10^7$	$\lambda_o \times 10^4$
10	-	-	0.2175	0.1305	0.83503	0.1299	0.83503	0.1299
20	-	-	0.2193	0.2607	0.8349	0.26066	0.8349	0.2606
30	-	-	0.2210	0.3906	0.8348	0.39132	0.8348	0.3913
40	-	-	0.2228	0.5201	0.8347	0.5219	0.8347	0.5219
50	-	-	0.2245	0.6492	0.8346	0.65256	0.8346	0.6525
60	-	-	0.2263	0.7780	0.83446	0.7831	0.83446	0.7831

Table 5 : Results of Isothermal Polymerization without gel effect

(Results in paranthesis are numerical computations with $\Delta t = 0.0001$ min)

Time	$[M] \times 10^{-7}$	$[P] \times 10^7$	$Q_1 \times 10^3$	Q_2	$\lambda_o \times 10^3$	λ_1	$\lambda_2 \times 10^{-4}$	PDI
10	0.8631	0.834	0.1745	0.7297	0.1306	0.3019	0.1386	1.9851
	(0.8632)	(0.834)	(0.1745)	(0.7297)	(0.1305)	(0.3016)	(0.1385)	(1.9864)
20	0.8340	0.8328	0.1686	0.6822	0.2608	0.5933	0.2682	1.9869
	(0.8341)	(0.8328)	(0.1686)	(0.6823)	(0.2607)	(0.5930)	(0.2680)	(1.9873)
30	0.8059	0.8317	0.1629	0.6379	0.3907	0.8746	0.3892	1.9879
	(0.8060)	(0.8317)	(0.1629)	(0.6380)	(0.3905)	(0.8741)	(0.3890)	(1.9882)
40	0.7788	0.8305	0.1574	0.5965	0.5203	1.1461	0.5022	1.9892
	(0.7788)	(0.8305)	(0.1574)	(0.5966)	(0.520)	(1.1454)	(0.5019)	(1.9895)
50	0.7526	0.8294	0.1521	0.5579	0.6495	1.4081	0.6077	1.9908
	(0.7527)	(0.8294)	(0.1521)	(0.5580)	(0.6492)	(1.4072)	(0.6074)	(1.9910)
60	0.7273	0.8283	0.1470	0.5218	0.7784	1.6610	0.7063	1.9929
	(0.7274)	(0.8283)	(0.1470)	(0.5219)	(0.7780)	(1.6599)	(0.7059)	(1.9930)

Table 6 : Results of Nonisothermal Polymerization without gel effect

(Results in paranthesis are numerical computations with $\Delta t = 0.0001 \text{ min}$)

$$U = 2.0343 \times 10^{-3} \frac{\text{Kcal}}{\text{hr cm}^2 \text{ } ^\circ\text{C}}$$

$$\text{Dia} = 2.0 \text{ cm}$$

Time (min)	Temp. $^\circ\text{K}$	$[\text{M}] \times 10^{-1}$ gmoles lit	$[\text{P}] \times 10^7$ gmoles lit	$Q_1 \times 10^3$	Q_2	$\lambda_0 \times 10^3$	λ_1	$\lambda_2 \times 10^4$	PDI
10	331.32	0.8687	0.6631	0.1707	0.8791	0.09047	0.2454	0.1329	1.9897
	(331.49)	(0.8662)	(0.7529)	(0.1707)	(0.7742)	(0.1142)	(0.2718)	(1.1332)	(1.9864)
20	331.27	0.8462	0.6575	0.1662	0.8595	0.1716	0.4714	0.2575	1.982
	(331.44)	(0.8405)	(0.749)	(0.1655)	(0.7315)	(0.2151)	(0.5218)	(0.2572)	(1.9863)
30	331.23	0.8244	0.6531	0.1617	0.8013	0.2515	0.6893	0.3755	1.9876
	(331.39)	(0.8159)	(0.7456)	(0.1605)	(0.6912)	(0.3191)	(0.7749)	(0.3738)	(1.987)
40	331.184	0.8034	0.6487	0.1575	0.7648	0.3303	0.900	0.4874	1.9874
	(331.342)	(0.7920)	(0.7423)	(0.1557)	(0.6531)	(0.4221)	(0.1013)	(0.4835)	(1.9874)
50	331.146	0.7830	0.6446	0.1534	0.7302	0.40809	0.1104	0.5936	1.9876
	(331.296)	(0.7689)	(0.7392)	(0.1510)	(0.6174)	(0.5242)	(0.1243)	(0.5868)	(1.9883)
60	331.110	0.7633	0.6407	0.1495	0.6772	0.4849	0.1301	0.6942	1.988
	(331.252)	(0.7467)	(0.7361)	(0.1466)	(0.5837)	(0.6254)	(0.1466)	(0.68403)	(1.989)

TABLE 7

Effect of Shear on Rate of Polymerisation in Absence of
Activated Carbon

[M] = 8.356 gmoles/lit

 ρ_m at 60°C = 0.869 gm/cc[I₂] = 0.0533 gmoles/lit ρ_{ps} at 60°C = 1.0475 gm/cc

RPM	$\gamma = \frac{\omega R_R}{R_G - R_R}$ sec ⁻¹	Slope $\frac{3}{x \times 10}$ lit/min	$Y \times 10^5$ $\frac{0.5 \text{ lit}}{0.5 \text{ gmoles min}}$	$r_p \times 10^4$ $\frac{\text{gmoles}}{\text{lit min}}$	$\frac{Z}{R}$
0	0.0	4.28	8.466	1.627	0.9995
50	36.48	3.89	7.902	1.514	0.9985
100	72.96	3.41	6.876	1.327	0.9917
130	94.85	3.19	6.407	1.245	0.9964
165	120.39	3.55	6.908	1.348	0.9988
200	145.92	3.76	7.451	1.430	0.9935
250	182.40	4.35	8.820	1.694	0.9991

TABLE 8

Effect of Shear on Rate of Polymerisation in Presence of
Activated Carbon

Carbon Concentration: 100 mg/200 ml monomer

$[M] = 8.356$ gmoles/lit

ρ_m at $60^\circ\text{C} = 0.869$ gm/cc

$[I_2] = 0.05275$ gmoles/lit

ρ_{ps} at $60^\circ\text{C} = 1.0475$ gm/cc

RPM	$\gamma = \frac{\omega R_R}{R_G - R_R}$ sec ⁻¹	Slope $\times 10^3$ lit/min	$Y \times 10^{0.5}$ lit gmoles min	$r_p \times 10^4$ gmoles lit min	R^2
0	0.0	5.0	10.17	1.940	0.9947
50	36.48	3.59	7.267	1.399	0.9995
75	54.72	4.19	9.017	1.711	0.9997
100	72.96	4.99	10.37	1.989	0.9850
150	109.44	4.63	9.307	1.800	0.9992
180	131.33	4.69	9.565	1.824	0.9968

TABLE 9

Effect of Activated Carbon (-350 mesh size) on
Rate of Polymerization

 $[M] = 8.356 \text{ gmoles/lit}$
 $\rho_{ps} \text{ at } 60^\circ\text{C} = 1.0475 \text{ gm/cc}$
 $\rho_m \text{ at } 60^\circ\text{C} = 0.869 \text{ gm/cc}$

$\frac{[C] \times 10^2 \text{ gmoles}}{\text{lit}}$	$\frac{1}{[C] \text{ lit gmoles}}$	$\frac{[I_2] \text{ gmoles}}{\text{lit}}$	$\frac{\text{Slope}_3 \times 10^3 \text{ lit}}{\text{min}}$	$Y \times 10^4$	$\frac{r_P \times 10^4 \text{ gmoles}}{\text{lit min}}$	$\frac{1}{r_P - r_{P0} \text{ lit min gmoles}}$	R^2
0	∞	0.037	3.868	0.983	1.580	-	0.997
1.66	60	0.038	4.582	1.114	1.826	40650.4	0.996
2.33	42.86	0.037	4.300	1.088	1.757	56657.2	0.999
2.66	37.50	0.038	4.560	1.085	1.773	51948.1	0.999
3.33	30.00	0.038	4.520	1.130	1.846	37664.2	0.998
6.00	16.67	0.037	5.220	1.331	2.133	18099.5	0.999

TABLE 10

Effect of Activated Carbon (-250 mesh size) on
Rate of Polymerization

[M] = 8.356 gmoles/lit

 ρ_{ps} at 60°C = 1.0475 gm/cc ρ_m at 60 C = 0.869 gm/cc

$\frac{[C]}{x 10^2}$ gmoles lit	$\frac{1}{[C]}$ lit gmoles	$[I_2]$ gmoles lit	Slope $\times 10^3$ lit min	$Y \times 10^4$	r_p $\times 10^4$ gmoles lit min	$\frac{1}{r_p - r_{p0}}$ lit min gmoles	R^2
0.00	∞	0.037	3.868	0.983	1.581	-	0.997
1.66	60	0.037	3.960	1.009	1.618	266666.7	0.999
2.00	50	0.037	3.952	1.010	1.615	289855.0	0.993
2.33	42.86	0.037	3.822	0.962	1.562	-	0.997
3.00	33.33	0.039	4.390	1.087	1.794	46838.4	0.999
3.66	27.27	0.038	4.170	1.047	1.704	80775.4	0.999

Table 11Gel and Glass effect constitutive equations

$$k_t = \frac{k_{to} D_o}{D_o + k_{to} \theta_t \lambda_o} \quad (\text{gel effect}) \quad (11.1)$$

$$k_p = \frac{k_{po} D_o}{D_o + k_{po} \theta_p \lambda_o} \quad (\text{glass effect}) \quad (11.2)$$

where

$$\theta_t = \frac{\theta_t^0 \exp(E_{\theta_t}/RT)}{[I_2]} \quad (11.3)$$

$$\theta_p = \theta_p^0 \exp(E_{\theta_p}/RT) \quad (11.4)$$

$$D_o = \left[\frac{2.303(1-\phi_p)}{A + B(1-\phi_p)} \right] \quad (11.5)$$

$$\gamma = \frac{k_{tc}}{k_{td}} = k_{\gamma}^0 \exp(E_{\gamma}/RT) \quad (11.6)$$